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Improved Fits for the Vibrational and Rotational Constants of Many States of Nitrogen and Oxygen

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All pertinent published measurements of the vibrational intervals $\Delta G(v+\frac{1}{2})$ and rotational constants B_v for 17 states of NITROGEN N_2, 4 states of N_2^+, the ground state of O_2, and 4 states of O_2^+ have been assembled and plotted against v. (These are the states important in modeling the fluorescence produced when air is bombarded by fast electrons.) ~~These~~ values of ΔG and B_v are compared with values calculated from the standard polynomials in powers of $v+\frac{1}{2}$, using the coefficients tabulated by Huber and Herzberg (1979). In about 70% of the states considered these tabulated coefficients do not give optimum fits of the basic spectroscopic data, usually because of new data published since 1979. In these cases new improved coefficients have been derived by ~~least-squares fitting. The results are tabulated and plotted.~~

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PREFACE

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CONVERSION TABLE

Conversion factors for U.S. customary to metric (SI) units of measurement

(Symbols of SI units given in parentheses in middle column)

To convert from	To	Multiply by
angstrom (Å)	meters (m)	$1.000\,000 \times 10^{-10}$
atmosphere (normal)	kilo pascal (kPa)	$1.013\,25 \times 10^{2}$
bar	kilo pascal (kPa)	$1.000\,000 \times 10^{2}$
barn	meters (m^2)	$1.000\,000 \times 10^{-28}$
British thermal unit (thermochemical)	joule (J)	$1.054\,350 \times 10^{3}$
calorie (thermochemical)	joule (J)	4.184 000
cal (thermochemical)/cm^2	mega joule/m^2 (MJ/m^2)	$4.184\,000 \times 10^{-2}$
curie	giga Becquerel (GBq)*	$3.700\,000 \times 10^{1}$
degree (angle)	radian (rad)	$1.745\,329 \times 10^{-2}$
degree Fahrenheit (°F)	degree kelvin (K)	$T_K = (T_{°F} + 459.67)/1.8$
electron volt	joule (J)	$1.602\,19 \times 10^{-19}$
erg	joule (J)	$1.000\,000 \times 10^{-7}$
erg/second	watt (W)	$1.000\,000 \times 10^{-7}$
foot	meter (m)	$3.048\,000 \times 10^{-1}$
foot-pound-force	joule (J)	1.355 818
gallon (U.S. liquid)	meter^3 (m^3)	$3.785\,412 \times 10^{-3}$
inch	meter (m)	$2.540\,000 \times 10^{-2}$
jerk	joule (J)	$1.000\,000 \times 10^{9}$
joule/kilogram (J/kg) (radiation dose absorbed)	Gray (Gy)**	1.000 000
kilotons	tera joules	4.183
kip (1000 lbf)	newton (N)	$4.448\,222 \times 10^{3}$
kip/inch^2 (ksi)	kilo pascal (kPa)	$6.894\,757 \times 10^{3}$
ktap	newton-second/m^2 ($N\text{-}s/m^2$)	$1.000\,000 \times 10^{2}$
micron	meter (m)	$1.000\,000 \times 10^{-6}$
mil	meter (m)	$2.540\,000 \times 10^{-5}$
mile (international)	meter (m)	$1.609\,344 \times 10^{3}$
ounce	kilogram (kg)	$2.834\,952 \times 10^{-2}$
pound-force (lbf avoirdupois)	newton (N)	4.448 222
pound-force inch	newton-meter (N-m)	$1.129\,848 \times 10^{-1}$
pound-force/inch	newton/meter (N/m)	$1.751\,268 \times 10^{2}$
pound-force/foot^2	kilo pascal (kPa)	$4.788\,026 \times 10^{-2}$
pound-force/inch^2 (psi)	kilo pascal (kPa)	6.894 757
pound-mass (lbm avoirdupois)	kilogram (kg)	$4.535\,924 \times 10^{-1}$
pound-mass-foot^2 (moment of inertia)	kilogram-meter^2 ($kg\text{-}m^2$)	$4.214\,011 \times 10^{-2}$
pound-mass/foot^3	kilogram/meter^3 (kg/m^3)	$1.601\,846 \times 10^{1}$
rad (radiation dose absorbed)	Gray (Gy)**	$1.000\,000 \times 10^{-2}$
roentgen	coulomb/kilogram (C/kg)	$2.579\,760 \times 10^{-4}$
shake	second (s)	$1.000\,000 \times 10^{-8}$
slug	kilogram (kg)	$1.459\,390 \times 10^{1}$
torr (mm Hg, 0° C)	kilo pascal (kPa)	$1.333\,22 \times 10^{-1}$

* The Becquerel (Bq) is the SI unit of radioactivity; 1 Bq = 1 event/s.

** The Gray (Gy) is the SI unit of absorbed radiation.

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SECTION 1
INTRODUCTION

In predicting or analyzing the radiation from disturbed or heated air, one often must deal with transitions among excited states of nitrogen and oxygen. In the aurora, for example, energetic charged particles inelastically scatter in the upper atmosphere to produce a myriad of highly excited electronic, vibrational, and rotational states of N_2, N_2^+, O_2, and O_2^+. These excited states can radiatively de-excite by making one or more transitions to successively less energetic states until ultimately the stable ground state is reached. As more sophisticated models are developed which include transitions among excited states with high vibrational levels, molecular constants valid for high vibrational levels are needed to accurately predict the wavelengths of these transitions, and to calculate quantities such as Franck-Condon factors which determine the relative rates of these transitions.

More than a decade has passed since the publication of Huber and Herzberg's book *Constants of Diatomic Molecules* (1979), Lofthus and Krupenie's monograph *The Spectrum of Molecular Nitrogen* (1977), and Krupenie's monograph *The Spectrum of Molecular Oxygen* (1972). These standard works have been extremely useful in many areas of geophysical research, as evidenced by the hundreds of published scientific reports in which references to these works are made. In the past ten years, however, new spectroscopic measurements have become available which affect some of the molecular constants published in these works. Frequently this is because the recent measurements extend to higher vibrational levels than the old ones. For example, Piper *et al.* (1989) pointed out inadequacies in the tabulated constants of Lofthus and Krupenie for the N_2 A and B states at high vibrational levels, and consequently used the constants determined by Roux *et al.* (1983). As another example, James *et al.* (1988) calculated Franck-Condon factors for the O_2^+ A–X band system for vibrational levels v' and $v'' = 0$ to 25 using the constants of Huber and Herzberg; the new data of Coxon and Haley (1984) make it possible to derive improved constants for these O_2^+ states.

The purpose of this report is to combine the most recent spectroscopic data with the older data in order to derive improved vibrational and rotational constants for several states of N_2, N_2^+, and O_2^+, as well as the ground state of O_2. Only those states that are important in modeling air fluorescence are covered. Some of these states are also important in modeling airglow phenonema; however, not all states involved in the airglow are included in this report, particularly the excited states of O_2. For these the interested reader may refer to an article by Slanger and Cosby (1988), who summarize recent vibrational and rotational data on the six lowest states of O_2.

SECTION 2
METHOD OF ANALYSIS

In the present work, for each molecular state the available spectroscopic data on vibrational energy intervals $\Delta G(v+\frac{1}{2})$, and rotational constants B_v, were compiled from published papers and plotted separately. In most of these papers vibrational energy intervals were not tabulated, and therefore had to be calculated. The vibrational energy interval is defined by

$$\Delta G(v+\tfrac{1}{2}) \equiv G(v+1) - G(v), \tag{1}$$

where $G(v)$ is the relative energy of the rotationless vibrational level v. Vibrational energy intervals of the upper (lower) state of a given band system are found by taking the difference between band origins of transitions with common lower (upper) levels, and upper (lower) levels separated by $\Delta v = 1$. For example, absorption measurements by Verma and Jois (1984) for N_2 b'–X band origins yielded 83,149.9 cm^{-1} for the 2-10 band, and 82,419.8 cm^{-1} for the 1-10 band. Hence the vibrational energy interval for the b' state between $v = 1$ and 2 is $\Delta G(\frac{3}{2}) = G(2) - G(1) = 730.1$ cm^{-1}. In some cases band head data, although not as accurate as band origin data, were used to calculate vibrational energy intervals as a means of extending the data to higher vibrational levels. Rotational constants B_v, on the other hand, are generally available from published reports so that derivation of these quantities by analysis of the rotational line positions was not required.

Before plotting $\Delta G(v+\frac{1}{2})$ and B_v, linear terms in v were added to these quantities in order to offset linear variations, so that the smaller nonlinear variations of these quantities with v could be displayed on an expanded plot scale. Thus the quantities $\Delta G(v+\frac{1}{2}) + pv$ and $B_v + qv$ are plotted against v in the figures, where p and q are constant coefficients that are chosen individually for each state.

In addition to the basic data, each graph includes one or more curves calculated from the standard polynomial expressions in $v+\frac{1}{2}$ (see Tables 1 and 2 for these expressions). In most cases a curve computed using the coefficients (molecular constants) of Huber and Herzberg (1979) is plotted. Curves computed using constants

published elsewhere, such as in Lofthus and Krupenie (1977), are also plotted when warranted. If none of these curves appears to give an optimum fit to the data now available, a new polynomial fit was made, using the method of least squares. The order of the polynomial was chosen so that the data are adequately represented by a minimum number of coefficients. In order to influence the fit in some cases, the more accurate measurements were given greater weight, and less accurate data were sometimes omitted from the fit entirely. A curve for each new fit is also plotted. By comparing the fits with the data shown in the figures, the general validity of the fits can be easily inferred.

Some molecular states have vibrational and rotational levels that are irregularly positioned off their normal course (e.g., Lofthus, 1960). Such states are said to be perturbed. These effects are most pronounced in many vibrational and rotational levels of the $b\ ^1\Pi_u$, $b'\ ^1\Sigma_u^+$, and $c_4'\ ^1\Sigma_u^+$ states of N_2. The spectroscopic data of these perturbed states are highly scattered, and not well represented by a smooth curve. Nevertheless, it is still useful to have fits to these data, even if approximate. In these cases, however, the method of least squares does not always give the best results. Therefore, when necessary, the data were fit by hand in order to achieve the desired results.

The recommended molecular constants based on these fits are presented in Tables 1 and 2 for nitrogen, and 3 and 4 for oxygen. The symbolic notation of the tabulated constants follows that of Huber and Herzberg (1979) and Lofthus and Krupenie (1977), except for the addition of some higher order terms as defined on the tables.

In this report, higher order terms in the rotational quantum number, such as $D_v J^2(J+1)^2$, are not considered because in most air fluorescence situations the rotational temperature is low enough that these terms can be neglected. New data on the values of D_v for many of the states are available, however, and may be found in the more recent references cited within this report.

Tables 1 and 3 include columns for T_0, which is the energy of an excited or ionic state relative to the $v = 0$, $J = 0$ level of the corresponding neutral ground state. T_0 is tabulated, rather than the equilibrium term value T_e, since T_0 is directly

measured and does not depend on the choice of vibrational constants ω_e, etc. The formula which relates T_0 to T_e is given on the tables. For most of the states, T_0 is derived from the ν_{00} band origins tabulated by Huber and Herzberg (1979), with the following exceptions: For the N_2 W state, T_0 is the sum of the term value of Cerny *et al.* (1980) for the W state relative to the A state and ν_{00} of Huber and Herzberg for the A–X transition. For the N_2 B' state, T_0 is the sum of ν_{00} of Roux and Michaud (1988) for the B'–B transition and ν_{00} of Huber and Herzberg for the B–X transition. The new values of T_0 for the N_2 W and B' states are within 1 cm^{-1} of the values of Huber and Herzberg. For the N_2 b' state, however, Verma and Jois (1984) measured $T_0 = 103678.3$ cm^{-1}, which is 4.5 cm^{-1} higher than the less accurate value quoted by Huber and Herzberg.

SECTION 3
RESULTS FOR NITROGEN

3.1 N_2 $X\ {}^1\Sigma_g^+$.

In Figure 1 vibrational data for the $X\ {}^1\Sigma_g^+$ state of N_2 from several investigations are plotted together with a curve computed using the constants listed by Huber and Herzberg (1979) and a curve resulting from a least squares fit of the data shown. The new fit agrees with that of Huber and Herzberg up to $v = 16$, but disagrees for higher levels. The difference between the two curves is a result of including the band head data of Herman (1945) for $v \geq 18$ in the new fit. The constants given by Huber and Herzberg were originally derived by Lofthus and Krupenie (1977), and are apparently based on data only for lower vibrational levels. The new vibrational constants are given in Table 1.

Figure 2 shows rotational data for the $X\ {}^1\Sigma_g^+$ state of N_2 from various sources. Similar, additional data not given in the figure are measurements of B_0 by Stoicheff (1954), Lofthus (1960), Vanderslice *et al.* (1965), and Butcher *et al.* (1971); less accurate measurements of B_v for $v = 0$ through 14 may be found in Watson and Koontz (1934) and Spinks (1942). The figure shows that the curve computed using the constants given by Huber and Herzberg (1979) fits the available data very well, and therefore a new fit is not necessary. Accordingly, the rotational constants of Huber and Herzberg are listed in Table 2.

3.2 N_2 $A\ {}^3\Sigma_u^+$.

The vibrational data of Dieke and Heath (1959), Tanaka and Jursa (1961), Roux *et al.* (1983), and Verma (1984) for the $A\ {}^3\Sigma_u^+$ state of N_2 are plotted in Figure 3. The more recent data are not substantially different from the older data, although their accuracy appears to be higher. Curves computed using the constants of Huber and Herzberg (1979), Roux *et al.*, and those obtained in this work are also given in Figure 3. The constants of Huber and Herzberg are from Lofthus and Krupenie (1977) (except for a sign error on $\omega_e y_e$ in Lofthus and Krupenie's tabulation), and are based on the data of Dieke and Heath. The constants of Roux *et al.* are based

only on their own measurements which do not go to vibrational levels as high a⌃ do Dieke and Heath's measurements. In the present work the band head dat· .of Tanaka and Jursa for $v > 13$ are included in the fit, in addition to the band origin data. This causes the new fit to fall off more rapidly than the previous fits for $v > 12$.

In Figure 4, various rotational data and three different fits are plotted for the $A\ ^3\Sigma_u^+$ state of N_2. The constants of Huber and Herzberg (1979) are from Lofthus and Krupenie (1977) which are based on the data of Miller (1966) and Dieke and Heath (1959). Again, the constants of Roux *et al.* are based only on their own measurements, which is one reason their fit differs from that of Huber and Herzberg. Close examination of Figure 4 reveals that their fit, despite the fact that it is one polynomial-order higher than that of Huber and Herzberg, does not fit their data at $v = 7$ and 8 very well. Inclusion of the recent measurements at higher v by Verma (1984) causes the new fit shown in the figure to turn downward more rapidly than the previous fits for $v > 10$. (The recent measurements of Carroll and Croke (1989) do not have as high an accuracy as Verma's, and hence were not included in the new fit.)

3.3 $N_2\ B\ ^3\Pi_g$.

The vibrational data of Dieke and Heath (1959), Roux *et al.* (1983), Verma (1984), and Roux and Michaud (1988) for the $B\ ^3\Pi_g$ state of N_2 are shown in Figure 5. The oldest of these measurements covers the largest number of vibrational levels. The fits of Cerny *et al.* (1980) and Roux *et al.* are based on their own high precision measurements which do not cover as many vibrational levels as Dieke and Heath. The constants of Huber and Herzberg (1979) are from Lofthus and Krupenie (1977); apparently these apply to only a limited range of vibrational levels and should not be employed above $v = 5$.

The B_v measurements of Dieke and Heath (1959), Roux *et al.* (1983), Verma (1984), and Carroll and Croke (1989) for the $B\ ^3\Pi_g$ state of N_2 are plotted in Figure 6. Other measurements not shown in the figure may be found in Budo (1937), Carroll (1952), and Carroll (1963) for $v = 3$, 4, and 11. The new fit, which is based on

the data plotted in Figure 6 except for the less accurate measurement of Carroll and Croke, differs from the fits of Huber and Herzberg (1979) and Roux *et al.* for $v > 12$ as seen in the figure, as a result of the more recent measurements of Verma.

3.4 N_2 W $^3\Delta_u$.

In Figures 7 and 8 the vibrational and rotational data of Cerny *et al.* (1980) and Roux and Michaud (1988) are plotted along with several fits. The linear curve in Figure 7 is based on the vibrational constants tabulated by Huber and Herzberg (1979) and Lofthus and Krupenie (1977), and was originally derived by Benesch and Saum (1971). Neither Huber and Herzberg nor Lofthus and Krupenie list rotational constants for the W $^3\Delta_u$ state of N_2. Cerny *et al.* measured N_2 W–B band origins and rotational structure for $v' \leq 7$, and derived constants based on these data. In later work Roux and Michaud extended the data base to $v' = 12$ and provided updated constants; however, in the course of the present work it was discovered that the values in their Table VIII do not fit their data for $G(v)$ and B_v. Therefore updated values, based on the new fits of the data shown in Figures 7 and 8, are listed in Tables 1 and 2.

3.5 N_2 B' $^3\Sigma_u^-$.

The vibrational and rotational data for the B' $^3\Sigma_u^-$ state of N_2 from several investigations are plotted in Figures 9 and 10, along with fits derived from constants given by Huber and Herzberg (1979), which are from Lofthus and Krupenie (1977), and from constants given by Roux and Michaud (1988), which are based on their own measurements but do not cover vibrational levels as high as do the measurements of Tilford *et al.* (1965b). As seen in the figures the fits of Huber and Herzberg are adequate; vibrational and rotational constants from this source are therefore tabulated in Tables 1 and 2.

3.6 N_2 a' $^1\Sigma_u^-$.

No new measurements of vibrational and rotational data for the a' $^1\Sigma_u^-$ state of N_2 have been published recently. The available data are plotted in Figures 11 and 12,

along with curves computed using the constants of Huber and Herzberg (1979). It is seen that the curves fit the data adequately. These constants are therefore recommended, and hence listed in Tables 1 and 2.

3.7 N_2 $a\ ^1\Pi_g$.

No new measurements of vibrational and rotational data for the $a\ ^1\Pi_g$ state of N_2 have been published recently (see Figures 13 and 14). Since the constants of Huber and Herzberg (1979) yield curves that fit the available data adequately, they are recommended and listed in the tables.

3.8 N_2 $w\ ^1\Delta_u$.

Figure 15 shows the available vibrational data for the $w\ ^1\Delta_u$ state of N_2, along with the fits of Huber and Herzberg (1979) and Lofthus and Krupenie (1977). The substantial disagreement between the two fits is the result of different data sets used in obtaining the fits. Lofthus and Krupenie fit a second order polynomial to the data of Lofthus and Mulliken (1957); Huber and Herzberg fit a linear equation to the band head data of Tanaka *et al.* (1964) which cover higher vibrational levels, but are lower in accuracy. Therefore, the latter fit is best for treating high vibrational levels, and hence the corresponding constants are listed in Table 1..

As can be seen in Figure 16 the curve computed using rotational constants of the $w\ ^1\Delta_u$ state of N_2 from Huber and Herzberg (1979) is an adequate fit of the available data, except for the anomalous measurement of McFarlane (1966). These constants are therefore listed in Table 2.

3.9 N_2 $C\ ^3\Pi_u$.

Dieke and Heath (1959) reported vibrational data for the $C\ ^3\Pi_u$ state of N_2 for $v = 0$–4 and derived vibrational constants. Tilford *et al.* (1965c) later determined band origins for the $C\ ^3\Pi_u$–$X\ ^1\Sigma_g^+$ 0-0, 1-0, and 2-0 bands. In addition they made slight revisions to the vibrational data of Dieke and Heath as a result of their analysis. Using these data they then determined new vibrational constants; Huber

and Herzberg (1979) include these updated constants in their tabulation. Figure 17 verifies that the curve computed using these constants is in good agreement with the data, and therefore these constants are included in Table 1.

Dieke and Heath (1959) also reported B_v values for this state for v = 0–4, and used these data to derive rotational constants. Tilford *et al.* (1965c) found good agreement between their own measurements of B_v and those of Dieke and Heath. The constants of Dieke and Heath are included in the tabulation of Huber and Herzberg (1979). It may be noted that the two highest order rotational constants listed in Lofthus and Krupenie (1977) for this state are in error. Figure 18 verifies that the curve computed using the constants tabulated in Huber and Herzberg is in good agreement with the data, and therefore these constants are included in Table 2.

3.10 N_2 $E\ ^3\Sigma_g^+$.

Only transitions from the $E\ ^3\Sigma_g^+$ state of N_2 with $v' = 0$ and 1 have been observed in emission studies (Herman, 1945; Freund, 1969), which indicates that predissociation probably occurs for the higher vibrational levels (Lofthus and Krupenie, 1977); no absorption study of this state has been carried out. In a study of the rotational structure of the $E\ ^3\Sigma_g^+$ state, Carroll and Doheny (1974) measured $B_0 = 1.9273$ cm^{-1}. Thus molecular data only for $v = 0$ and 1 of this state are available. Since the $E\ ^3\Sigma_g^+$ state of N_2 is the first member of a Rydberg series which converges to N_2^+ $X\ ^2\Sigma_g^+$ (Lefebvre-Brion and Moser, 1965), it is assumed here that the variation of ΔG and B_v with vibrational level is the same as for N_2^+ $X\ ^2\Sigma_g^+$ (which is discussed in Section 3.18). The consequent approximate vibrational and rotational constants are listed in parentheses in Tables 1 and 2, respectively.

3.11 N_2 $C'\ ^3\Pi_u$.

In Figure 19 the vibrational data of Ledbetter and Dressler (1976), Carroll (1963), and Tanaka and Jursa (1961) for the $C'\ ^3\Pi_u$ state of N_2 are plotted with curves computed from the constants listed by Huber and Herzberg (1979), and those derived in this report. The constants of Huber and Herzberg are from Ledbetter and

Dressler who used a deperturbed value for the $v = 1$ level of the C' state in their analysis, as there is a strong homogeneous interaction between the $C'\ ^3\Pi_u$ ($v = 1$) and $C\ ^3\Pi_u$ ($v = 5$) states. The new fit shown in Figure 19 uses the observed value of Ledbetter and Dressler rather than the deperturbed value, so that the corresponding constants will predict the observed rather the deperturbed level. The vibrational constants based on the new fit shown in Figure 19 are given in Table 1.

The rotational data for the $C'\ ^3\Pi_u$ state of N_2 observed for $v = 0$ by Carroll (1963) and for $v = 1$ by Ledbetter and Dressler (1976) are plotted in Figure 20. According to Ledbetter and Dressler a rotational analysis has not yet been done for $v = 2$. Ledbetter and Dressler also computed a deperturbed value for $v = 1$ of $B_1 = 1.026$ cm^{-1}. Huber and Herzberg (1979) list in their table just the B_0 of Carroll (1963). In Figure 20 a new fit to the available observed data is also shown. The rotational constants that correspond to the new fit are given in Table 2.

Because of the perturbation an unusually large value for $\omega_e x_e$ and a negative value for α_e are derived here for the $C'\ ^3\Pi_u$ state.

3.12 $N_2\ b\ ^1\Pi_u$.

Owing to the presence of perturbations in many levels of the $b\ ^1\Pi_u$ state of N_2, the vibrational data shown in Figure 21 for $v < 10$ are highly scattered and not easily fit to a simple polynomial. The data show that ΔG increases with v for low vibrational levels, which leads to a negative value for $\omega_e x_e$ in the new fit. Huber and Herzberg (1979) just list in their table the $\Delta G(\frac{1}{2})$ of Carroll and Collins (1969). Not shown in Figure 21 are the data of Yoshino *et al.* (1975) for $v = 7$, 9, 12, and 15, which are only very slightly different from the measurements of Carroll and Collins. Leoni (1972) and Leoni and Dressler (1972) give deperturbed vibrational and rotational constants for this state. Vibrational constants based on the new fit shown in Figure 21 are given in Table 1.

The rotational data for the $b\ ^1\Pi_u$ state of N_2, which are also scattered due to perturbations, are plotted in Figure 22. Included also in the figure is a new fit of the data. Huber and Herzberg (1979) list in their table just the B_0 of Carroll and

Collins (1969). In Table 2 are listed rotational constants which correspond to the new fit shown in Figure 22.

3.13 N_2 $D\ ^3\Sigma_u^+$.

No $\Delta G(\frac{1}{2})$ data for this state are available since only the $v = 0$ level of the $D\ ^3\Sigma_u^+$ state of N_2 has been observed. From rotational analysis Gero and Schmid (1940) obtained a value of $B_0 = 1.961$ cm^{-1}. This value is tabulated in both Huber and Herzberg (1979) and Lofthus and Krupenie (1977).

The $D\ ^3\Sigma_u^+$ state of N_2, like the $E\ ^3\Sigma_g^+$ state discussed above in Section 3.10, is also the first member of a Rydberg series which converges to N_2^+ $X\ ^2\Sigma_g^+$ (Lefebvre-Brion and Moser, 1965). Thus, in the same way as was done in Section 3.10, it is assumed for this state that the variation of $\Delta G(v + \frac{1}{2})$ and B_v with vibrational level is the same as for N_2^+ $X\ ^2\Sigma_g^+$ (which is discussed in Section 3.18). The consequent approximate vibrational and rotational constants are listed in parentheses in Tables 1 and 2, respectively.

3.14 N_2 $b'\ ^1\Sigma_u^+$.

Figures 23 and 24 show vibrational and rotational data, respectively, for the $b'\ ^1\Sigma_u^+$ state of N_2. According to Carroll *et al.* (1970) almost all levels of this state are perturbed, by the $c_4'\ ^1\Sigma_u^+$ state below $v = 17$ and by the $c_5'\ ^1\Sigma_u^+$ state for higher v, which makes the data in the figures highly scattered. Not shown in Figure 24 are the $v \leq 5$ rotational data of Wilkinson and Houk (1956) and Setlow (1948) which are similar to the data of Carroll *et al.* In addition to the data in Figures 23 and 24, new fits to the data, and curves computed using the deperturbed constants of Leoni (1972) and Leoni and Dressler (1972), which are tabulated in both Huber and Herzberg (1979) and Lofthus and Krupenie (1977), are plotted. The new fit of the vibrational data is simply a straight line fit to the $\Delta G(\frac{1}{2})$ of Verma and Jois (1984) and the $\Delta G(11\frac{1}{2})$ of Carroll *et al.*; the new fit of the rotational data is simply the constant value $B_v = 1.142$ cm^{-1}, which corresponds to the B_0 of Verma and Jois.

3.15 N_2 c_4' $^1\Sigma_u^+$.

Figures 25 and 26 show vibrational and rotational data for the c_4' $^1\Sigma_u^+$ state of N_2. Also shown in the figures are new fits to the data, and curves computed using the deperturbed constants of Leoni (1972) and Leoni and Dressler (1972), which are tabulated in both Huber and Herzberg (1979) and Lofthus and Krupenie (1977). Similar data not plotted in Figure 25 can be found in Worley (1943), Gaydon (1944), Lofthus (1957), Tilford and Wilkinson (1964), Yoshino and Tanaka (1977), Yoshino *et al.* (1979), and Roncin *et al.* (1987). Measurements of B_0 similar to those of Carroll *et al.* and Yoshino and Tanaka have also been obtained by Worley, Gaydon, and Lofthus. Vibrational and rotational constants that correspond to the new fits are listed in Tables 1 and 2, respectively.

3.16 N_2 x $^1\Sigma_g^-$.

No new measurements of vibrational and rotational data for the x $^1\Sigma_g^-$ state of N_2 have been published recently (see Figures 27 and 28). Since the constants of Huber and Herzberg (1979) yield curves that fit the available data adequately, they are listed in the tables.

3.17 N_2 y $^1\Pi_g$.

New fits to the observed data for the y $^1\Pi_g$ state of N_2 are plotted in Figures 29 and 30, with corresponding molecular constants listed in Tables 1 and 2. The data show that both $\Delta G(v + \frac{1}{2})$ and B_v increase with v from $v = 0$ to $v = 1$ due to the strong interaction present between the y $^1\Pi_g$ and k $^1\Pi_g$ states (Carroll and Subbaram, 1975), and this leads to negative values of $\omega_e x_e$ and α_e in the new fits. Both Huber and Herzberg (1979) and Lofthus and Krupenie (1977) tabulate the deperturbed constants of Carroll and Subbaram; curves derived from these constants are also given in the figures for comparison with the new fits.

3.18 $N_2^+ \; X\,^2\Sigma_g^+$.

Vibrational data from several investigations for the $X\,^2\Sigma_g^+$ state of N_2^+ are available for $v \leq 36$, and are plotted in Figure 31. The measured values of ΔG of Colbourn and Douglas (1977), Benesch *et al.* (1980), and Miller *et al.* (1984), which are not shown in the figure, are very close to those of Klynning and Pages (1972) for $v \leq 1$. Also not plotted are the similar measurements of Carroll (1959) for $v \leq 13$. A curve calculated using constants from the tabulation of Huber and Herzberg (1979), and a new fit of the data are also plotted in the figure. The new fit deviates significantly from the previous fit above $v = 10$ as can be seen in the figure. The new vibrational constants for this state are listed in Table 1.

The currently available rotational data for high vibrational levels from various studies also make it possible to improve the rotational constants for this state. The new fit shown in Figure 32 is substantially different from the curve computed using the constants tabulated in Huber and Herzberg (1979) which are derived from a linear fit to the rotational data at low v. For $v \leq 10$ only the data of Klynning and Pages (1972) and Miller *et al.* (1984) were included in the new fit. Similar data which are not shown in the figure are the measurements of Childs (1932), Carroll (1959), Colbourn and Douglas (1977), and Madina (1981). The new rotational constants are listed in Table 2.

3.19 $N_2^+ \; A\,^2\Pi_u$.

The vibrational constants listed in Huber and Herzberg (1979) for the $A\,^2\Pi_u$ state of N_2^+ are from Janin *et al.* (1963), and could not be improved upon here (see Figure 33). These constants are therefore given in Table 1.

Although no recent measurements have been made at high v, the rotational data of Janin *et al.* (1963) and Klynning and Pages (1972) for the $A\,^2\Pi_u$ state of N_2^+ can be used to extend the rotational constants up to $v = 14$. The new fit plotted in Figure 34 can be compared with the curve computed from the constants of Huber and Herzberg (1979) which were obtained through a linear fit of B_2 and B_3 of Colbourn and Douglas. For clarity the measurement of B_4 of Hansen *et al.* (1983a)

is omitted from the figure; however, it is very close to the measurement of Miller *et al.* (1984). The new rotational constants for this state are listed in Table 2.

3.20 N_2^+ $B\,^2\Sigma_u^+$.

Vibrational and rotational data for the $B\,^2\Sigma_u^+$ state of N_2^+ are available to quite high vibrational levels, as shown in Figures 35 and 36. The variation of ΔG and B_v with v is unusual, due to the interaction of this state with the $C\,^2\Sigma_u^+$ state (see Lofthus and Krupenie (1977), p. 165). Huber and Herzberg (1979) list vibrational constants which fit the data very well for $v \leq 9$ but deviate rapidly for higher v. In the present work, a new fit has been derived which fits the data moderately well up to $v = 28$, even though it is less accurate than Huber and Herberg's fit for low v (see Figure 35). A similar fit to B_v is shown in Figure 36. Huber and Herzberg just list B_0 in their table, so no corresponding curve is included in this figure. The value for B_0 derived by Madina (1981), which is close to those shown in Figure 36, is not plotted.

3.21 N_2^+ $C\,^2\Sigma_u^+$.

The vibrational constants of Huber and Herzberg (1979) for the $C\,^2\Sigma_u^+$ state of N_2^+ adequately fit the available data, as seen in Figure 37. These constants are therefore given in Table 1.

Figure 38 shows a new fit to the rotational data of Setlow (1948), Wilkinson (1956), and Carroll (1959) for the $C\,^2\Sigma_u^+$ state of N_2^+, for data up to $v = 6$. Huber and Herzberg (1979) just list the B_0 of Carroll in their table, so no corresponding curve is plotted for comparison. The new fit shown in Figure 38 is similar to the curve in Figure 4 of Carroll, who did not compute rotational constants since their data require a fit with more curvature at low v than at high v, and this would result in anomalous constants. The new fit gives a fair approximation of the data. The resulting rotational constants, which are listed in Table 2, do not exhibit any anomalies.

SECTION 4
RESULTS FOR OXYGEN

4.1 $O_2\ X\ ^3\Sigma_g^-$.

Albritton *et al.* in work never published but with results quoted in Krupenie (1972), studied the pertinent spectroscopic data available in 1971 and determined the best values for $G(v)$ up to $v = 21$ using a weighted least-squares fit. These values are plotted in Figure 39. At about the same time Snopko (1970) made new spectroscopic measurements for $v = 3$–7 and obtained ΔG values that agree very well with those of Albritton *et al.* (see Figure 39). Later, an extensive set of measurements was made by Creek and Nicholls (1975), from which they derived $G(v)$ values up to $v = 28$. As shown in Figure 39, a majority of their values agree quite well with older values. However, several of their values between $v = 6$ and 17 deviate significantly, and do not follow a smooth curve, as first noted by Copeland *et al.* (1987). Copeland *et al.* also obtained new spectroscopic data for $v = 9$–11 which disagree with the deviant values of Creek and Nicholls, and generally agree with the older data. Above $v = 21$ the only available ΔG data are the values of Creek and Nicholls, and a few old approximate values from Herman *et al.* (1961). In this region the Creek and Nicholls values are probably fairly accurate, because they follow a smooth curve and tend to be supported by the approximate values of Herman *et al.*

Albritton *et al.* also derived vibrational constants from the data for $v = 0$–21; these constants are reproduced in Krupenie (1972) and Huber and Herzberg (1979). The resulting ΔG curve is plotted in Figure 39. For $v > 20$ it deviates significantly from the more recent values of Creek and Nicholls (1975). Consequently, we have made a new least-squares fit, including all of the data shown in Figure 39 except the deviant Creek and Nicholls values at $v = 6$, 10, and 12, and the approximate values of Herman *et al.* (1961). The resultant curve is shown in Figure 39, and the constants listed in Table 3.

Krupenie (1972) has tabulated B_v values derived by a variety of investigators. These values are plotted in Figure 40, along with values from Herman *et al.* (1961),

Snopko (1970), Creek and Nicholls (1975), and Copeland *et al.* (1987). The results of Snopko lie significantly below the other results, for unknown reasons. The results of the older investigations are scattered around the relatively smooth curve followed by the values of Creek and Nicholls.

Rotational constants for this state have been tabulated by Krupenie (1972) and by Huber and Herzberg (1979), based on an unpublished analysis by Albritton *et al.* The corresponding curve, shown in Figure 40, fits the new data of Creek and Nicholls (1975) fairly well up to $v = 14$, but deviates significantly for higher v. Consequently, we have made a new least-squares fit of the Creek and Nicholls values (except the discordant point at $v = 5$) and two of the values of Copeland *et al.* (1987), omitting $v = 11$. This new fit is shown in Figure 40, and the corresponding constants listed in Table 4.

4.2 O_2^+ X $^2\Pi_g$.

Until the recent work of Coxon and Haley (1984), few accurate spectroscopic data on this state were available. Figures 41 and 42 depict ΔG and B_v values obtained from the Coxon and Haley analysis, as well as curves calculated from the spectroscopic constants that they derived (after correcting obvious sign errors in their values for $\omega_e z_e$ and δ_e). The curves are seen to fit the basic data very well, so the corresponding constants are listed in Tables 3 and 4. For comparison, linear curves calculated from the constants listed by Huber and Herzberg (1979) are also shown. These constants are based on older spectroscopic data, and do not yield very good fits to the newer data.

4.3 O_2^+ a $^4\Pi_u$.

In Figure 43 band origin data from Krupenie (1972), Cosby *et al.* (1980), Hansen *et al.* (1981), and Hansen *et al.* (1983b) are plotted. In addition curves computed using the vibrational constants of Huber and Herzberg (1979) and Hansen *et al.* (1983b) are given [after correcting the $\omega_e u_e$ value of Hansen *et al.* by a factor of 10 (P. C. Cosby, private communication, 1990)]. The latter curve is the best fit, and hence corresponding vibrational constants are given in Table 3.

Rotational data and fits from several reports are plotted in Figure 44 for the $a\,^4\Pi_u$ state of O_2^+. The recent, more accurate measurements of Hansen *et al.* (1983b) extend the data base up to $v = 7$ for this state. The rotational constants that they deduced by fitting the data are given in Table 4 [note that their γ_e value has been corrected by a factor of 10 (P. C. Cosby, private communication, 1990)].

4.4 O_2^+ $A\,^2\Pi_u$.

Curves computed using the molecular constants of Huber and Herzberg (1979) for the $A\,^2\Pi_u$ state of O_2^+ are plotted in Figures 45 and 46. Coxon and Haley (1984) presented high resolution band origins for this state, but not vibrational constants; therefore these data are fit here (see Figure 45 for a plot of this curve). They did, however, present rotational constants, but these do not fit the data very well above $v = 10$ (see Figure 46); therefore a new fit was computed using the method of least squares, where the anomalous value of B_1 of Coxon and Haley, probably due to a typographical error, was omitted from the fit (Figure 46). The recommended vibrational and rotational constants for this state are listed in Tables 3 and 4, respectively.

4.5 O_2^+ $b\,^4\Sigma_g^-$.

In Figure 47 band origin data from Krupenie (1972), Cosby *et al.* (1980), Hansen *et al.* (1981), and Hansen *et al.* (1983b) are plotted for the $b\,^4\Sigma_g^-$ state of O_2^+. In addition curves computed using the vibrational constants of Huber and Herzberg (1979) and Hansen *et al.* (1983b) are plotted. The fit of Huber and Herzberg was originally fit to $v \leq 3$ by Albritton *et al.* (unpublished), and tabulated in Krupenie (1972). The curve based on the vibrational constants of Hansen *et al.* (1983b) fits the data best for $v \leq 5$; that the data for $v = 6$ and 7 of Hansen *et al.* (1981) are less accurate than the data for $v \leq 5$ is a plausible explanation for the deviation of these points from the more recent curve. The vibrational constants of Hansen *et al.* (1983b) are listed in Table 3.

The available rotational data for the $b\,^4\Sigma_g^-$ state of O_2^+, from Nevin (1940), LeBlanc (1963), Cosby *et al.* (1980), and Hansen *et al.* (1983b), are plotted in Figure 48.

In addition curves computed using the constants of Huber and Herzberg (1979), which are also listed in Krupenie (1972), and Hansen *et al.* (1983b) are plotted in Figure 48 for comparison. The newer measurements are significantly more accurate than those of LeBlanc which do not fall on the plotted curves. The rotational constants based on the fit of Hansen *et al.* are listed in Table 4.

SECTION 5

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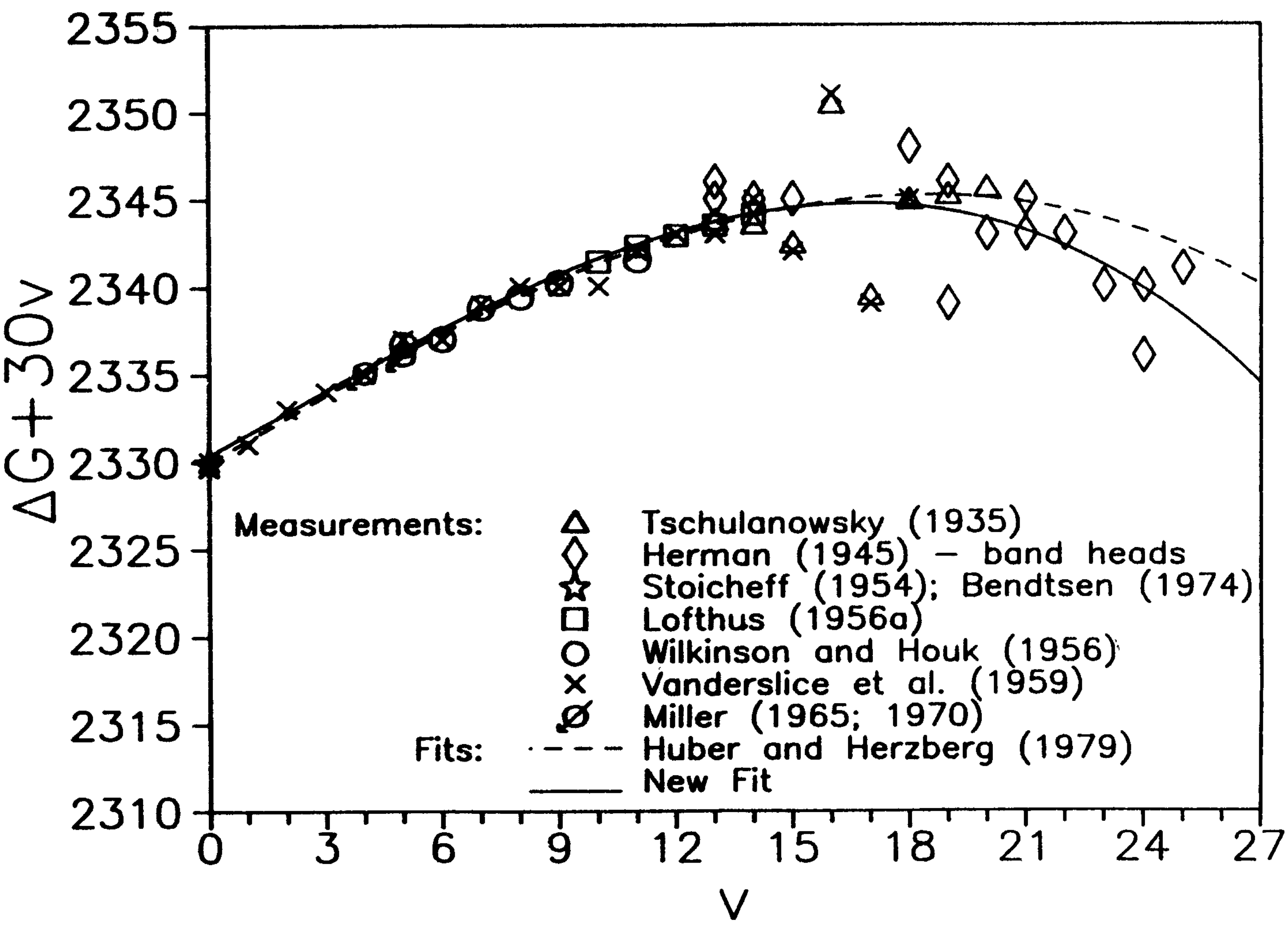

Figure 1. Vibrational data and fits for the $X\ {}^1\Sigma_g^+$ state of N_2.

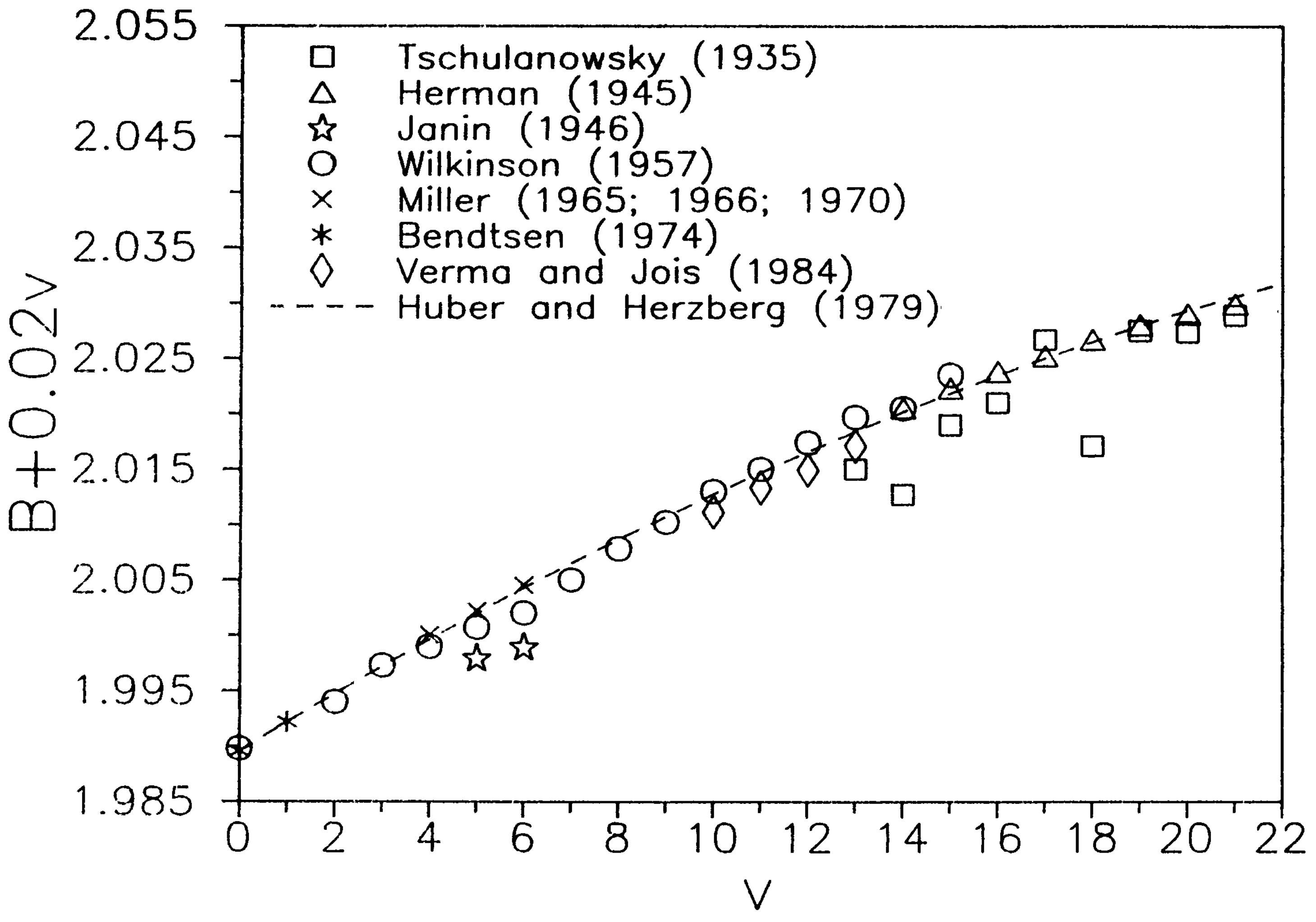

Figure 2. Rotational data and fit for the $X\ ^1\Sigma_g^+$ state of N_2.

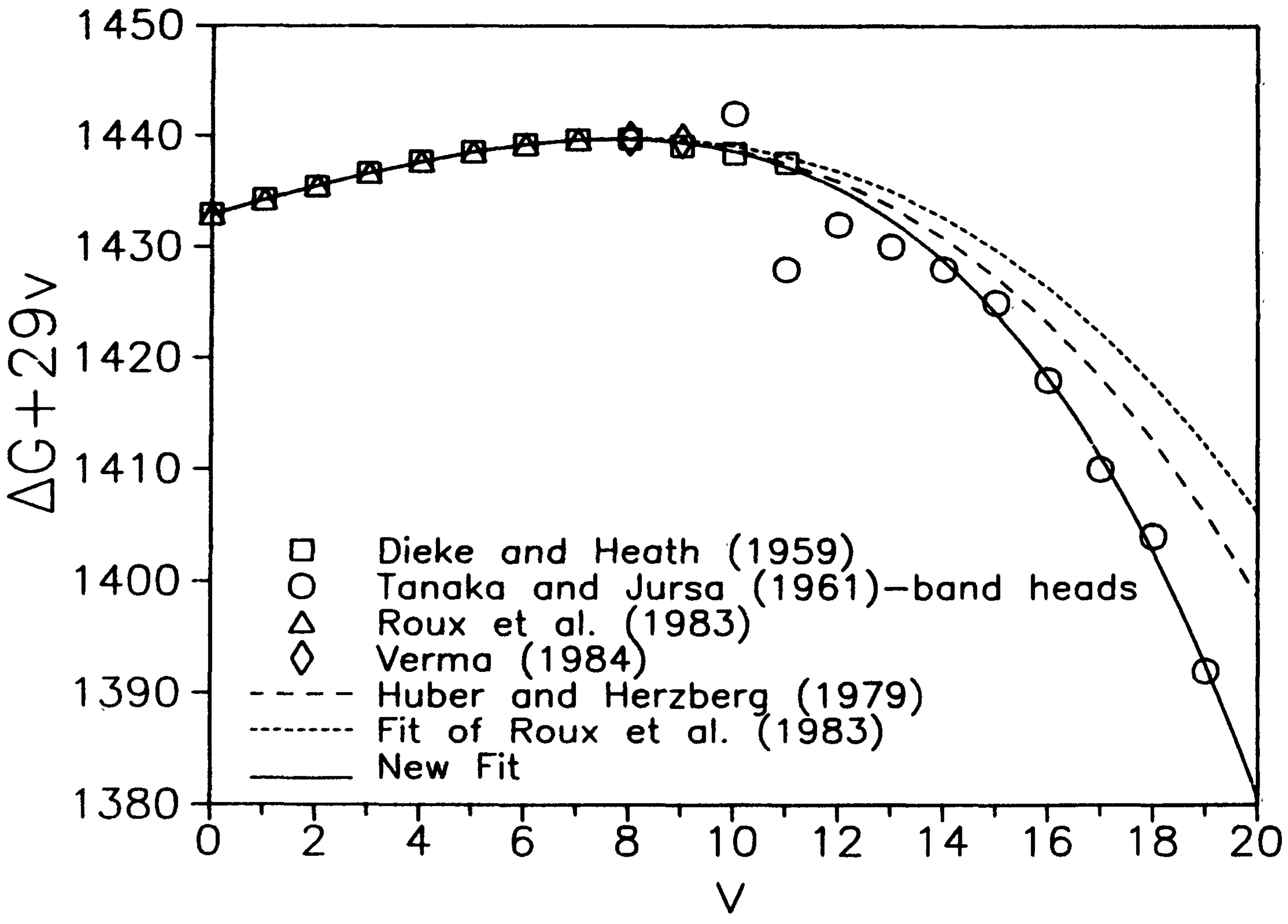

Figure 3. Vibrational data and fits for the $A\ ^3\Sigma_u^+$ state of N_2.

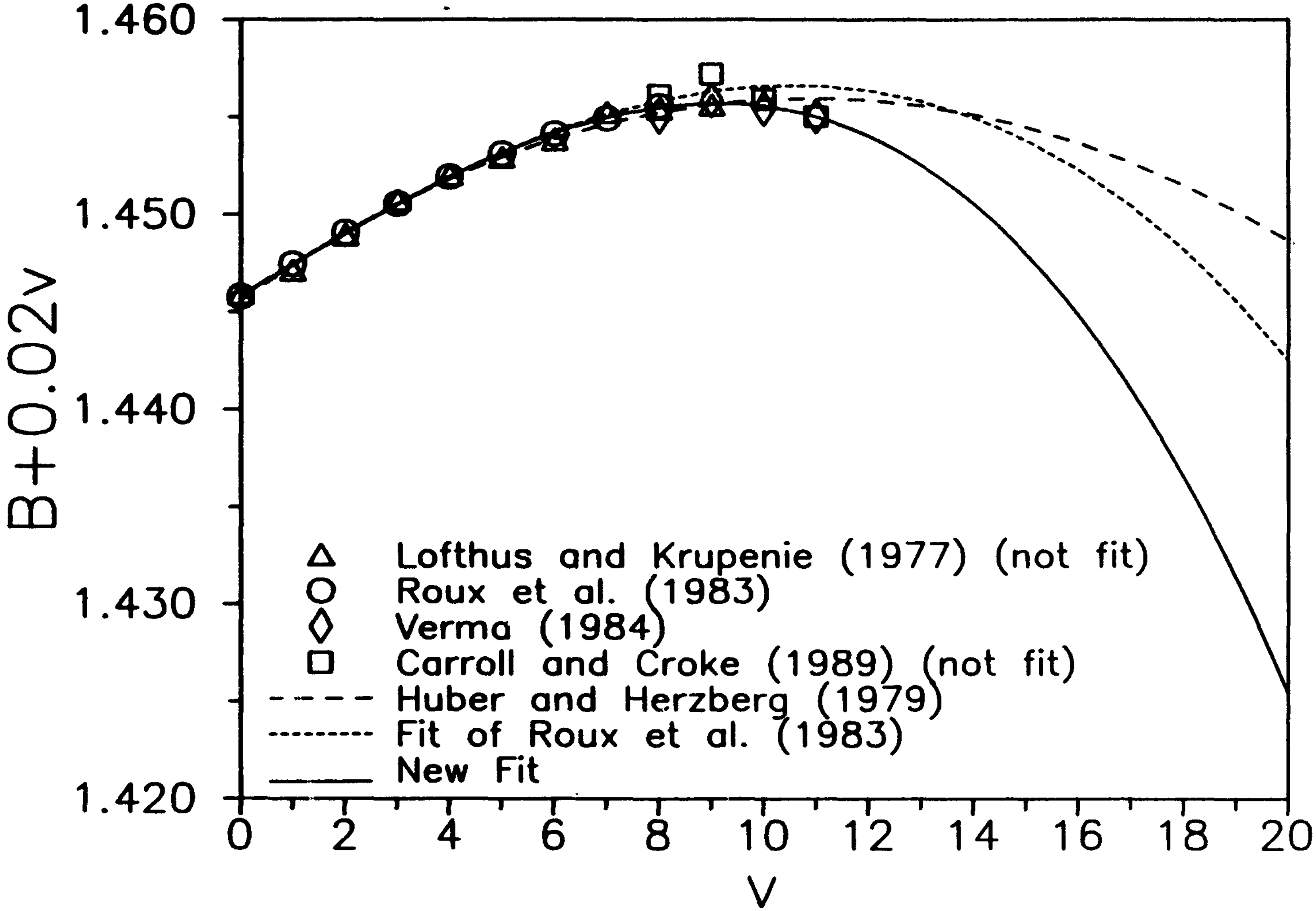

Figure 4. Rotational data and fits for the $A\,^3\Sigma_u^+$ state of N_2.

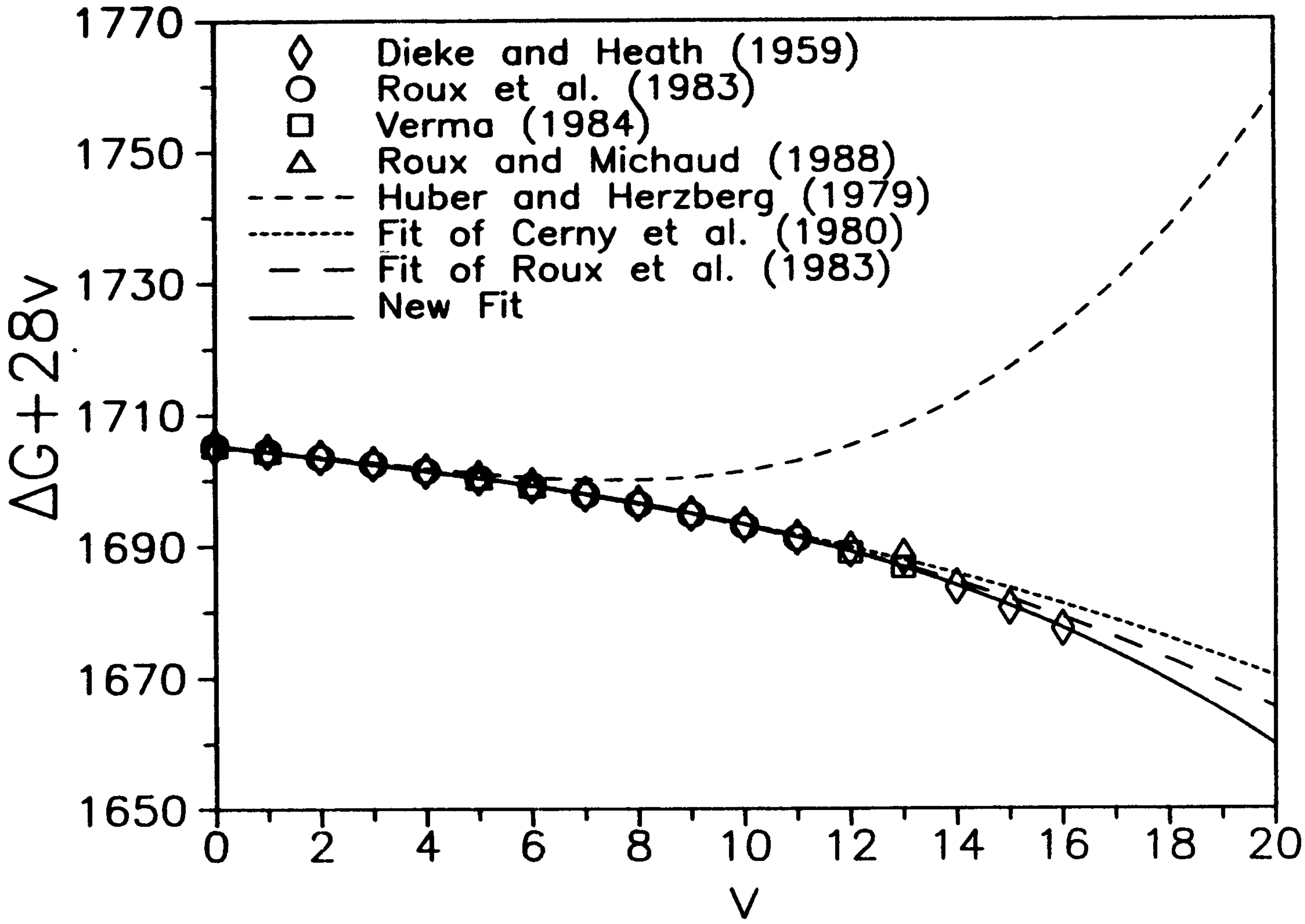

Figure 5. Vibrational data and fits for the $B\ ^3\Pi_g$ state of N_2.

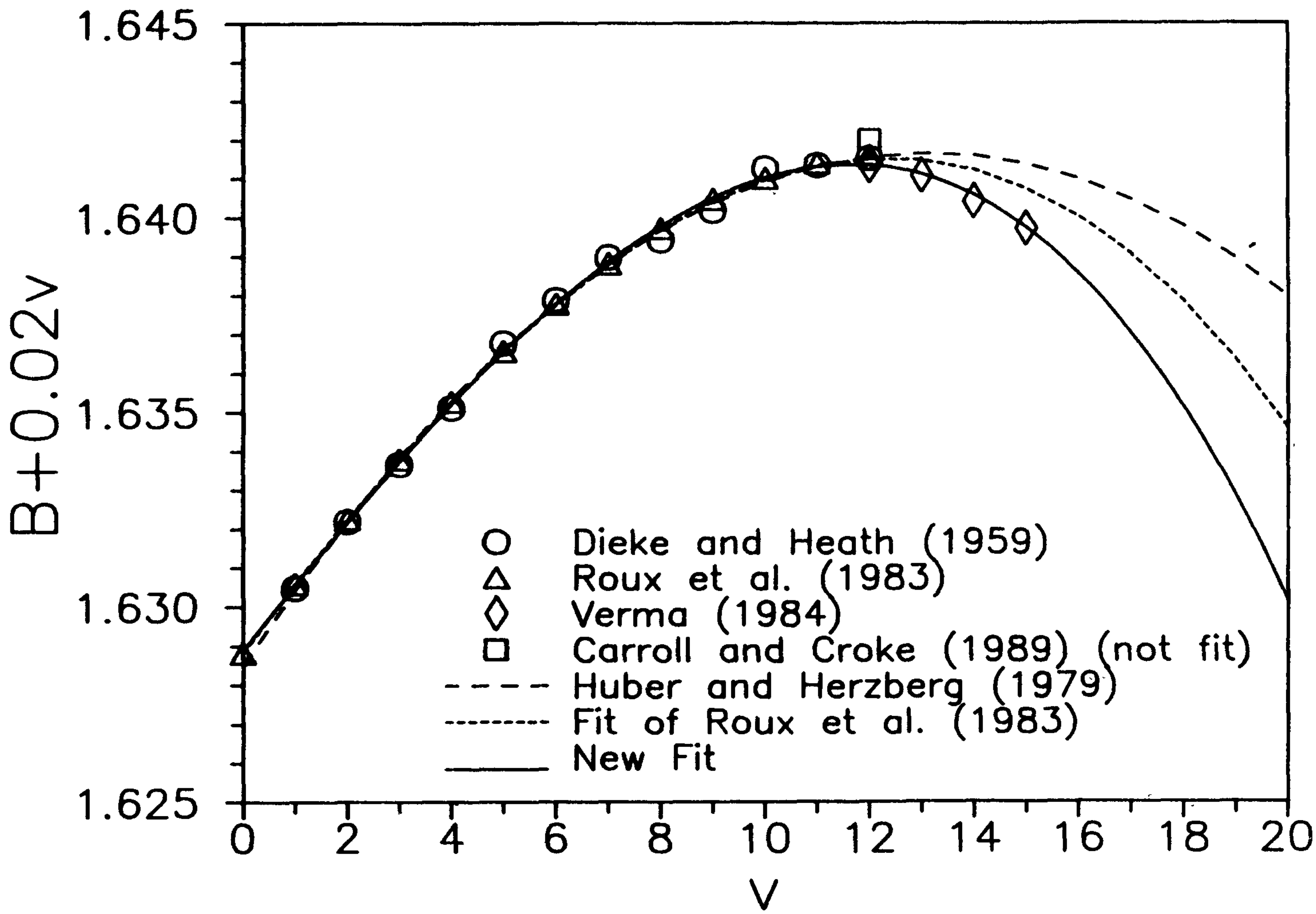

Figure 6. Rotational data and fits for the $B\ ^3\Pi_g$ state of N_2.

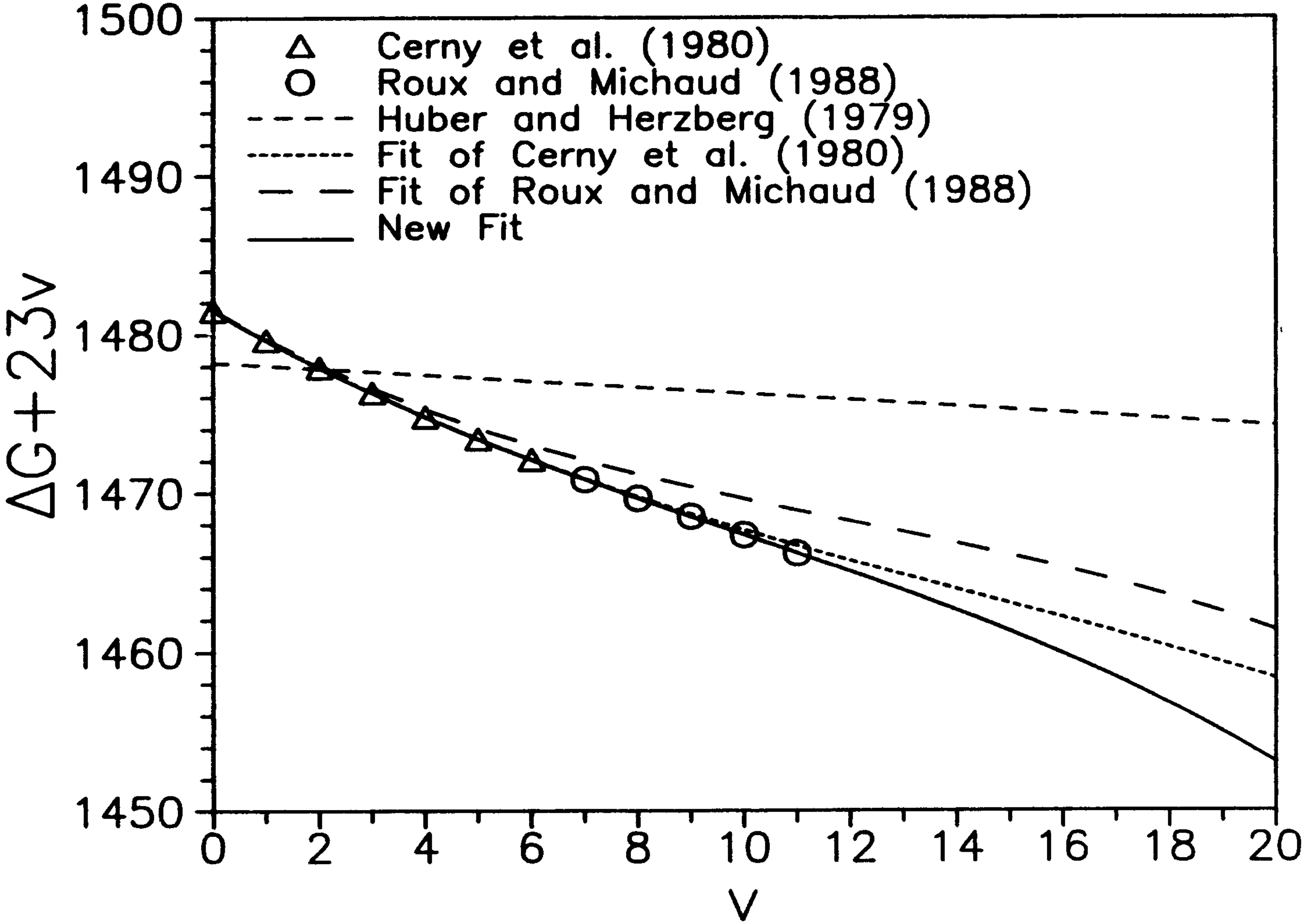

Figure 7. Vibrational data and fits for the $W\ ^3\Delta_u$ state of N_2.

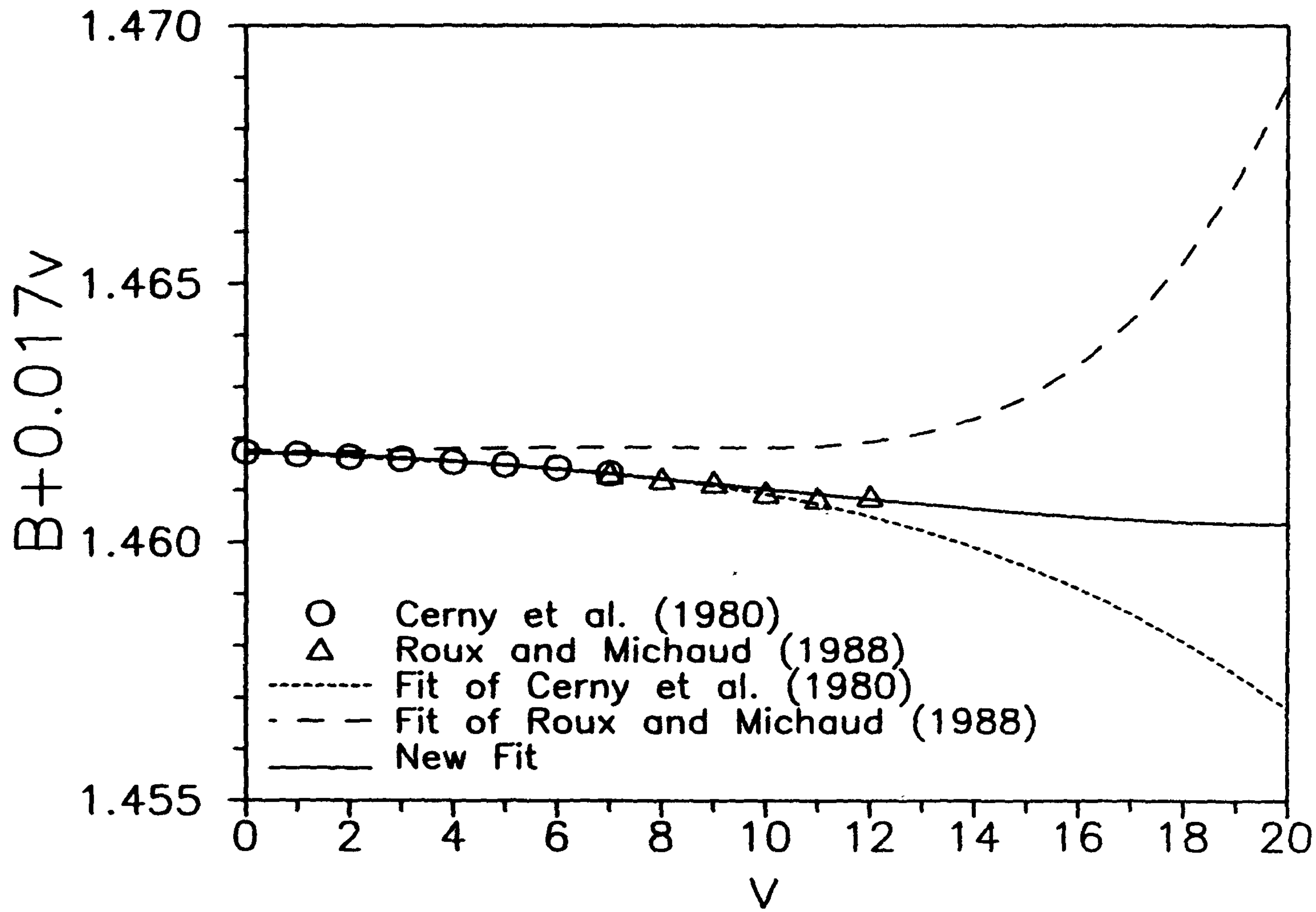

Figure 8. Rotational data and fits for the $W\ ^3\Delta_u$ state of N_2.

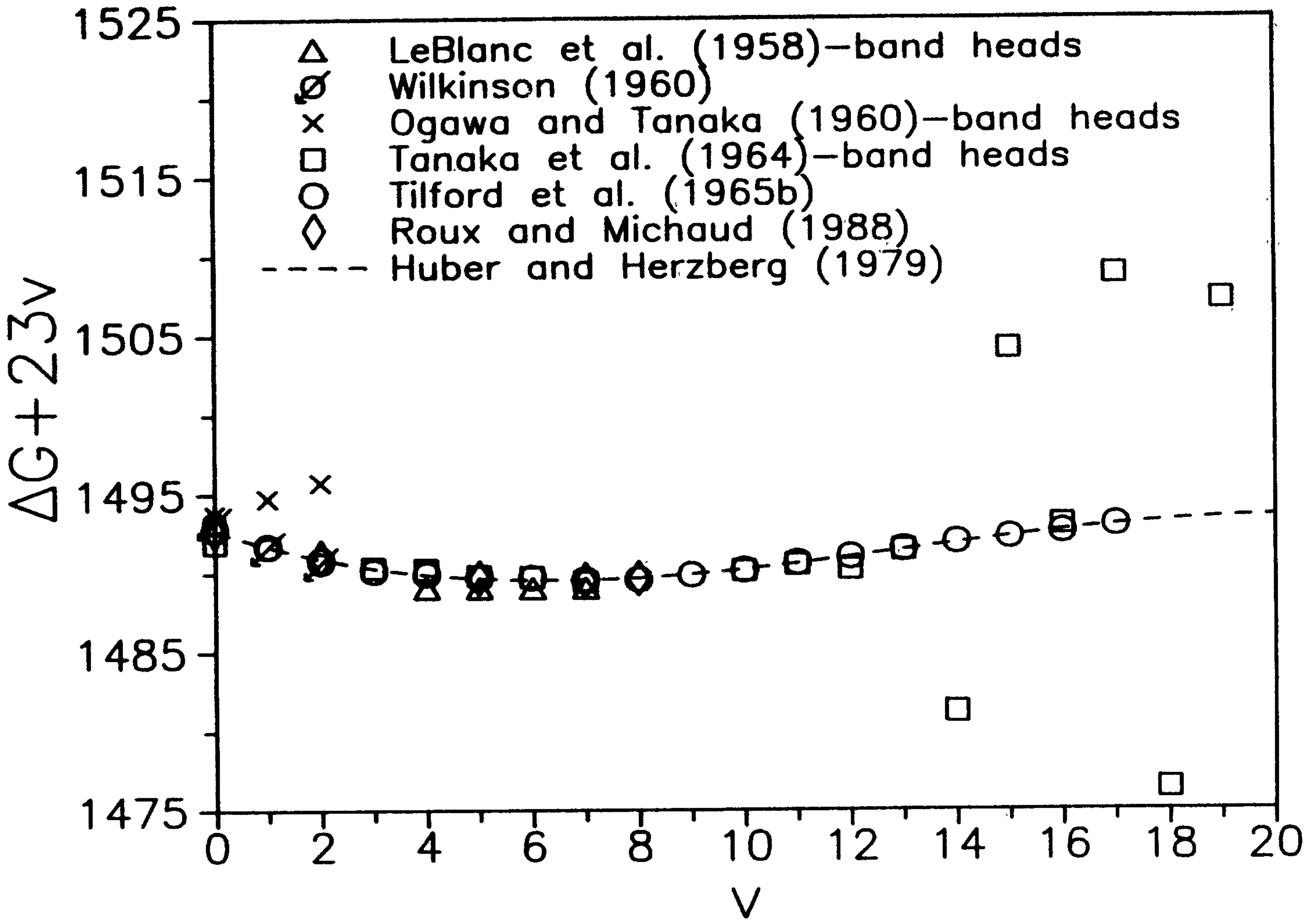

Figure 9. Vibrational data and fit for the $B'\ ^3\Sigma_u^-$ state of N_2.

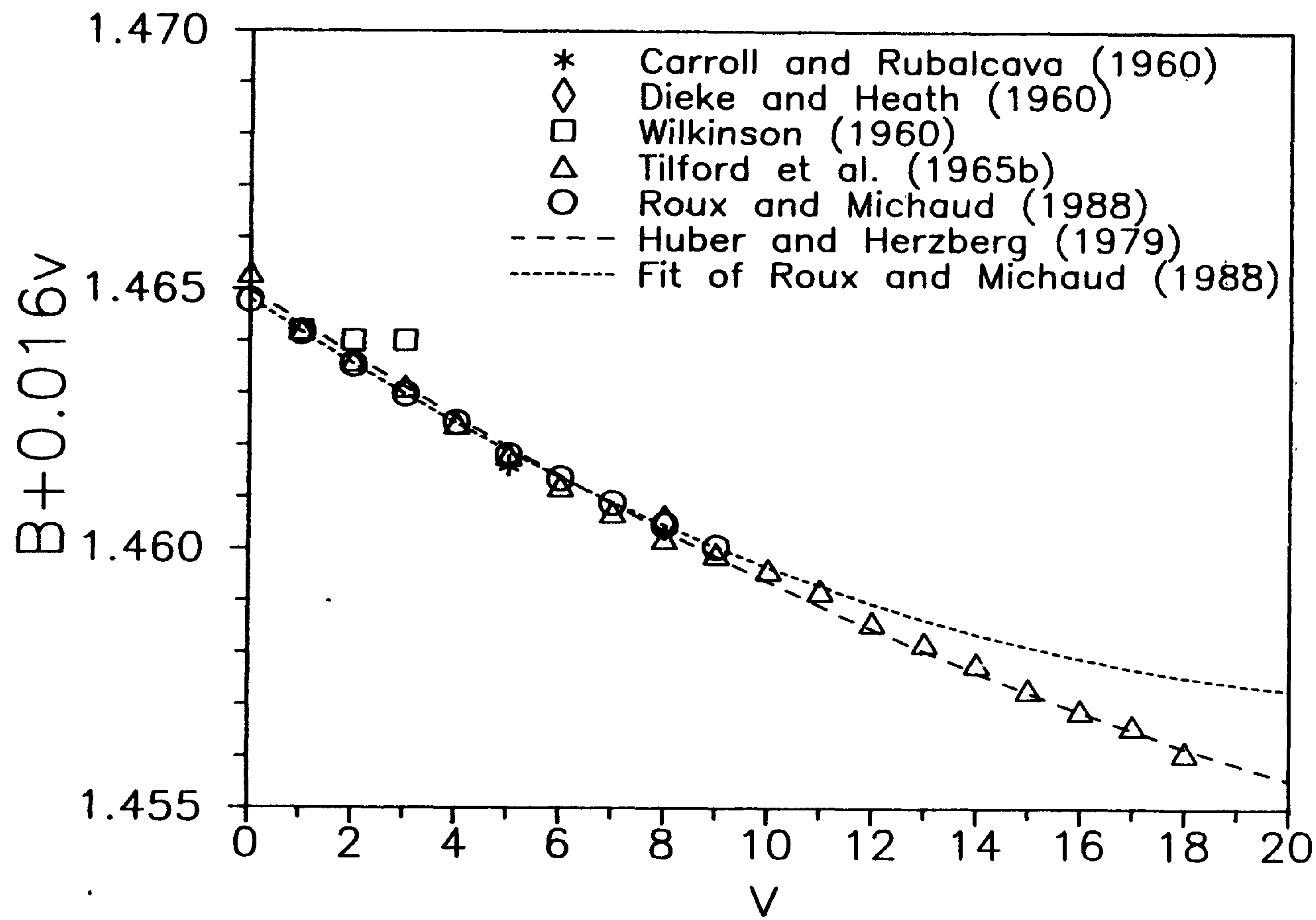

Figure 10. Rotational data and fits for the $B'\,^3\Sigma_u^-$ state of N_2.

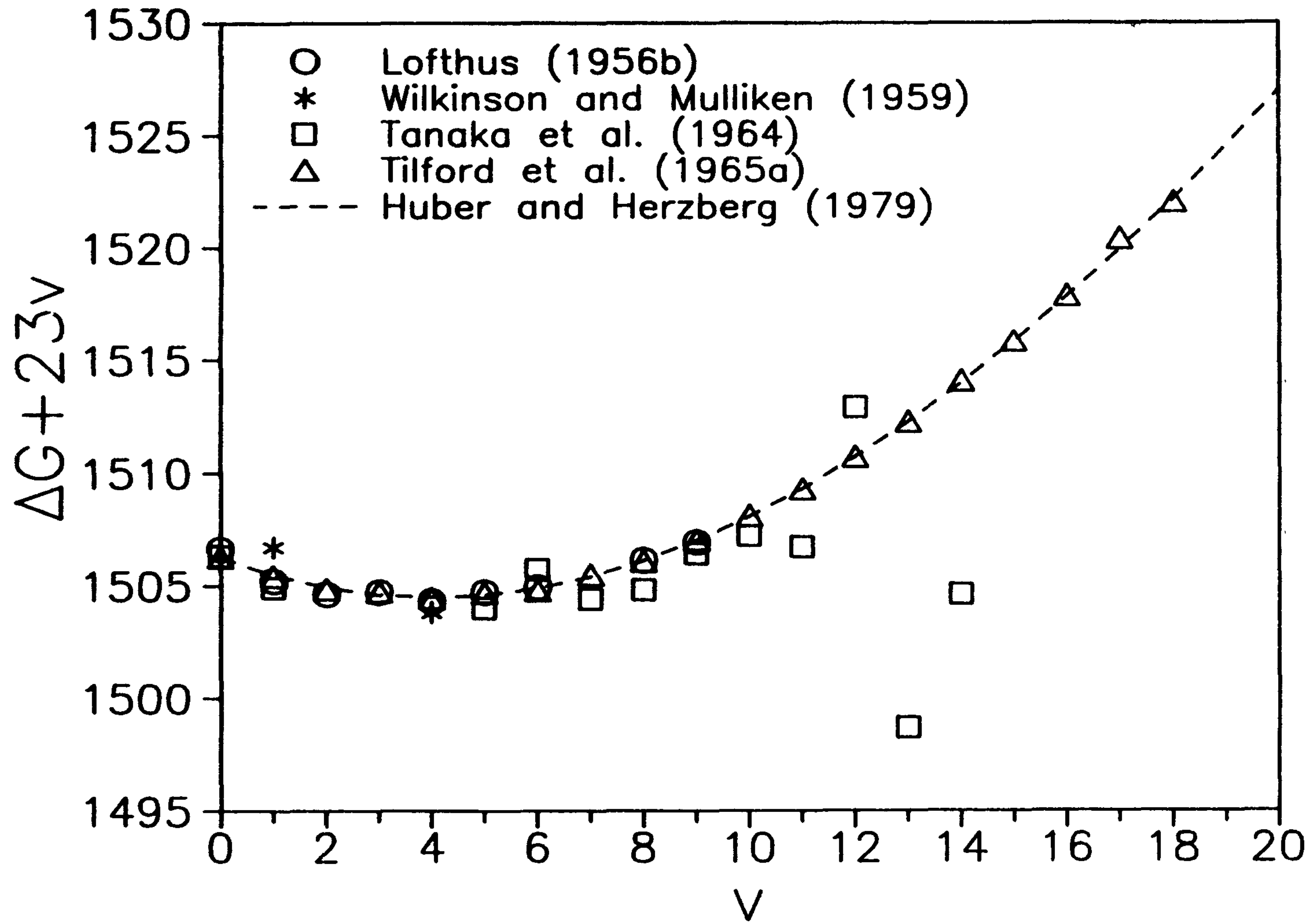

Figure 11. Vibrational data and fit for the $a'\ ^1\Sigma_u^-$ state of N_2.

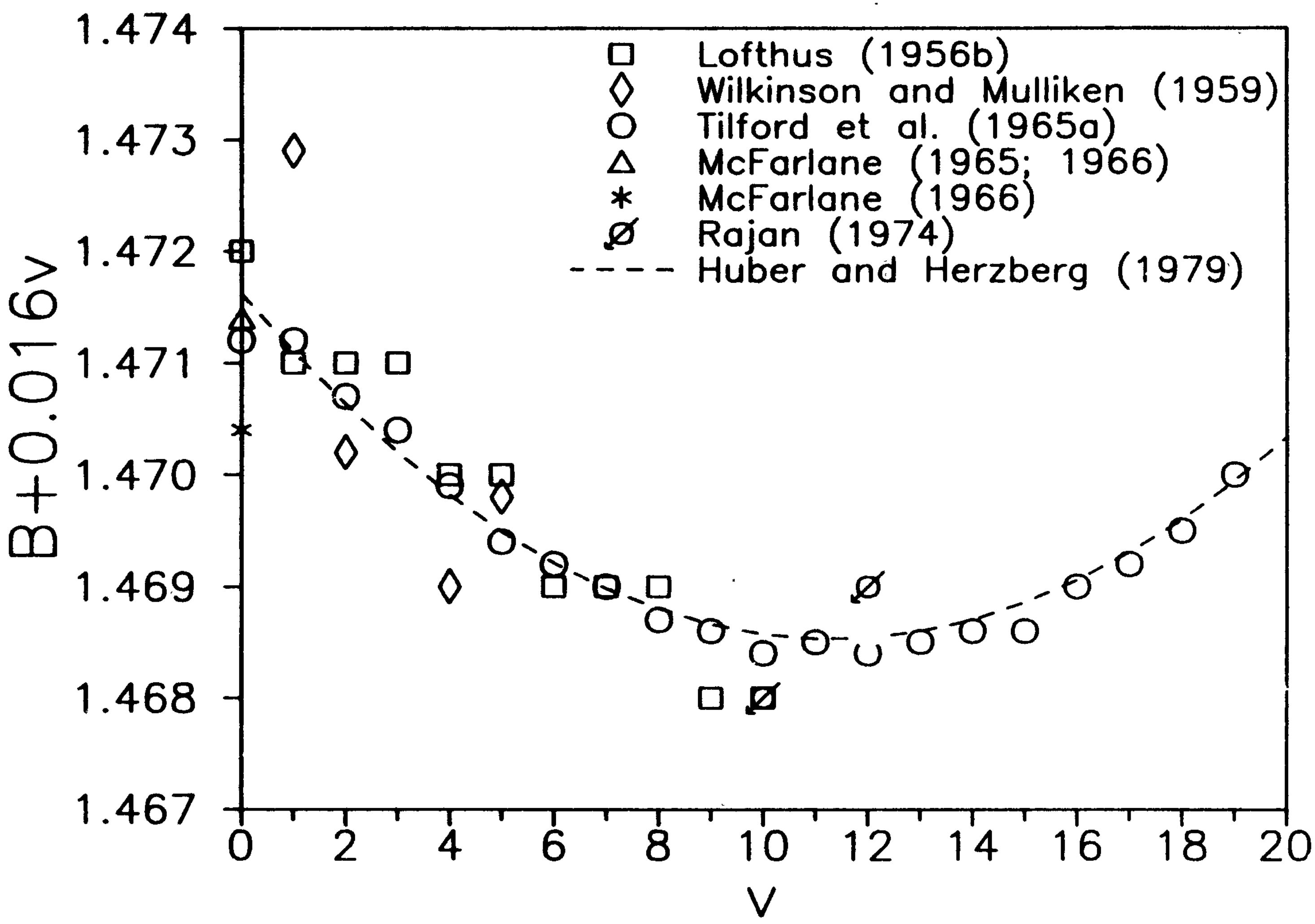

Figure 12. Rotational data and fit for the $a'\ ^1\Sigma_u^-$ state of N_2.

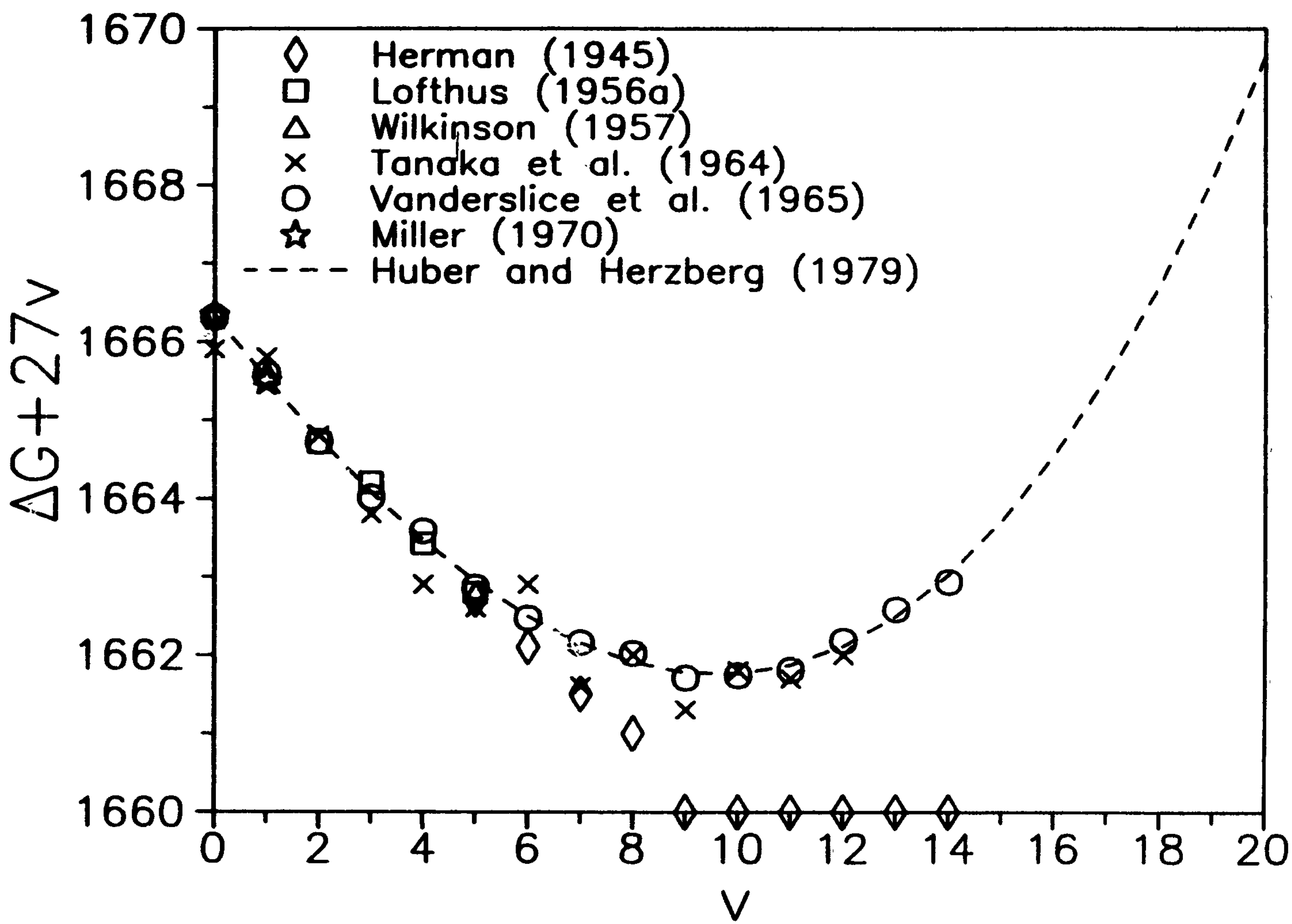

Figure 13. Vibrational data and fit for the $a\ ^1\Pi_g$ state of N_2.

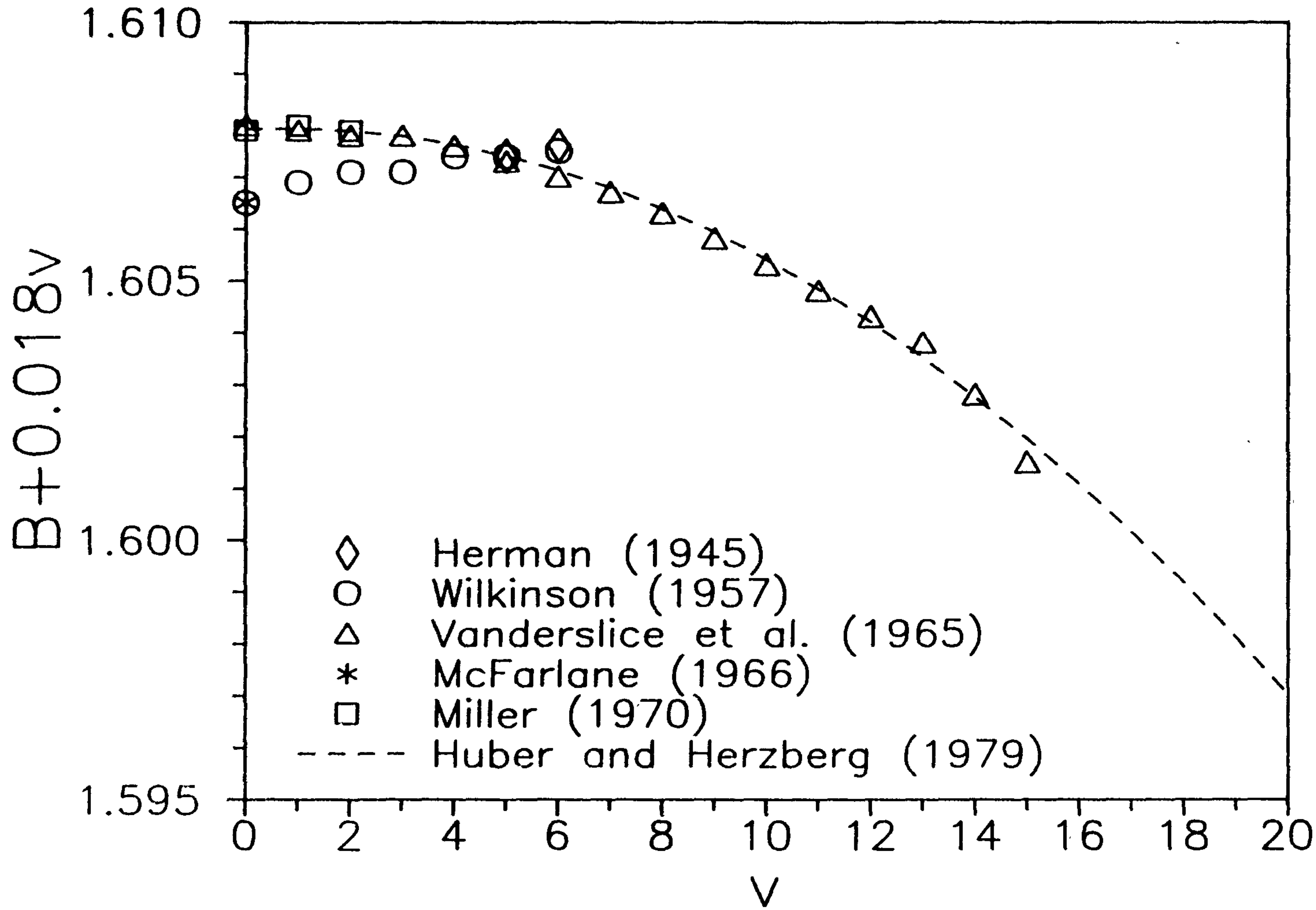

Figure 14. Rotational data and fit for the $a\ ^1\Pi_g$ state of N_2.

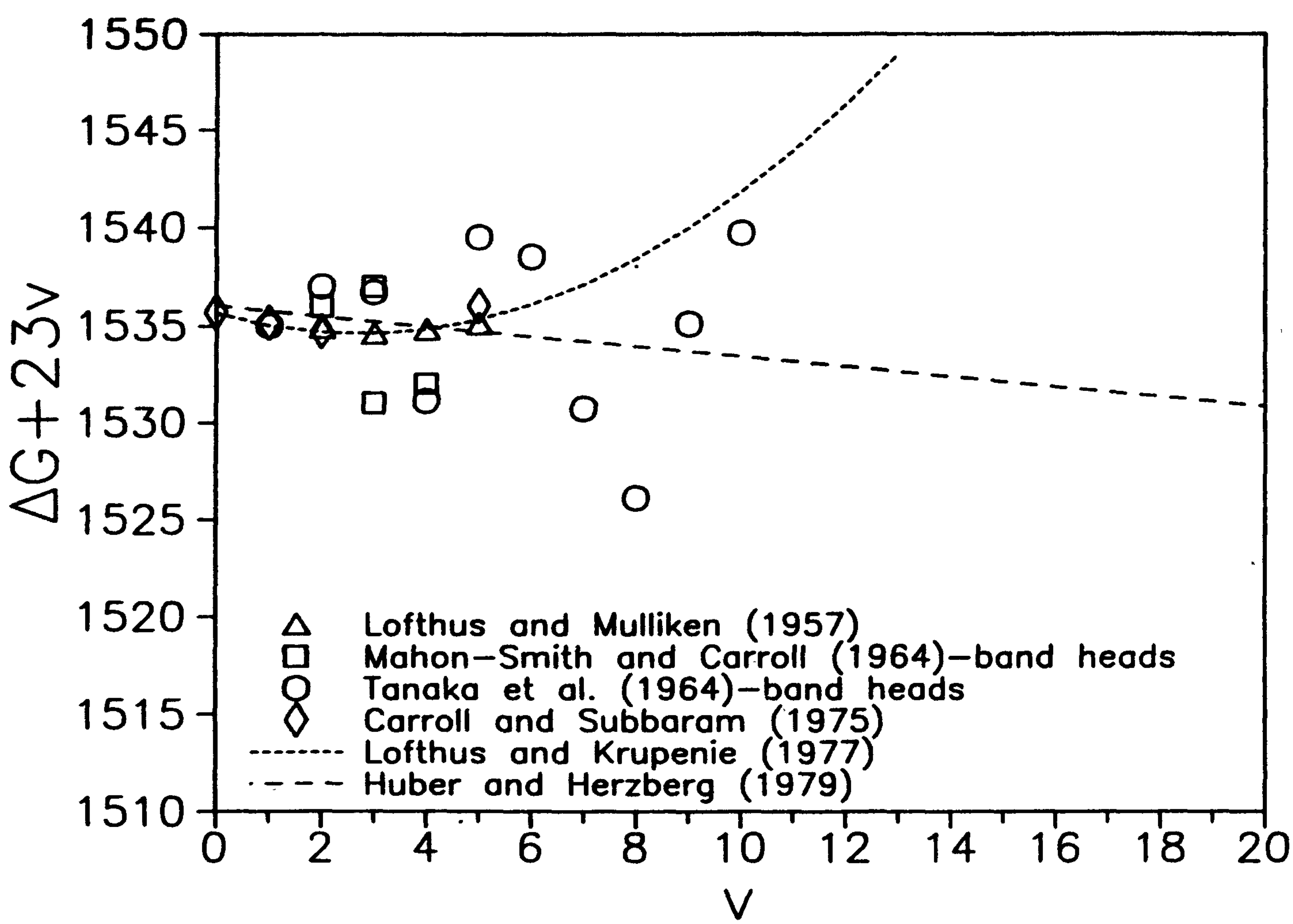

Figure 15. Vibrational data and fits for the $w\ ^1\Delta_u$ state of N_2.

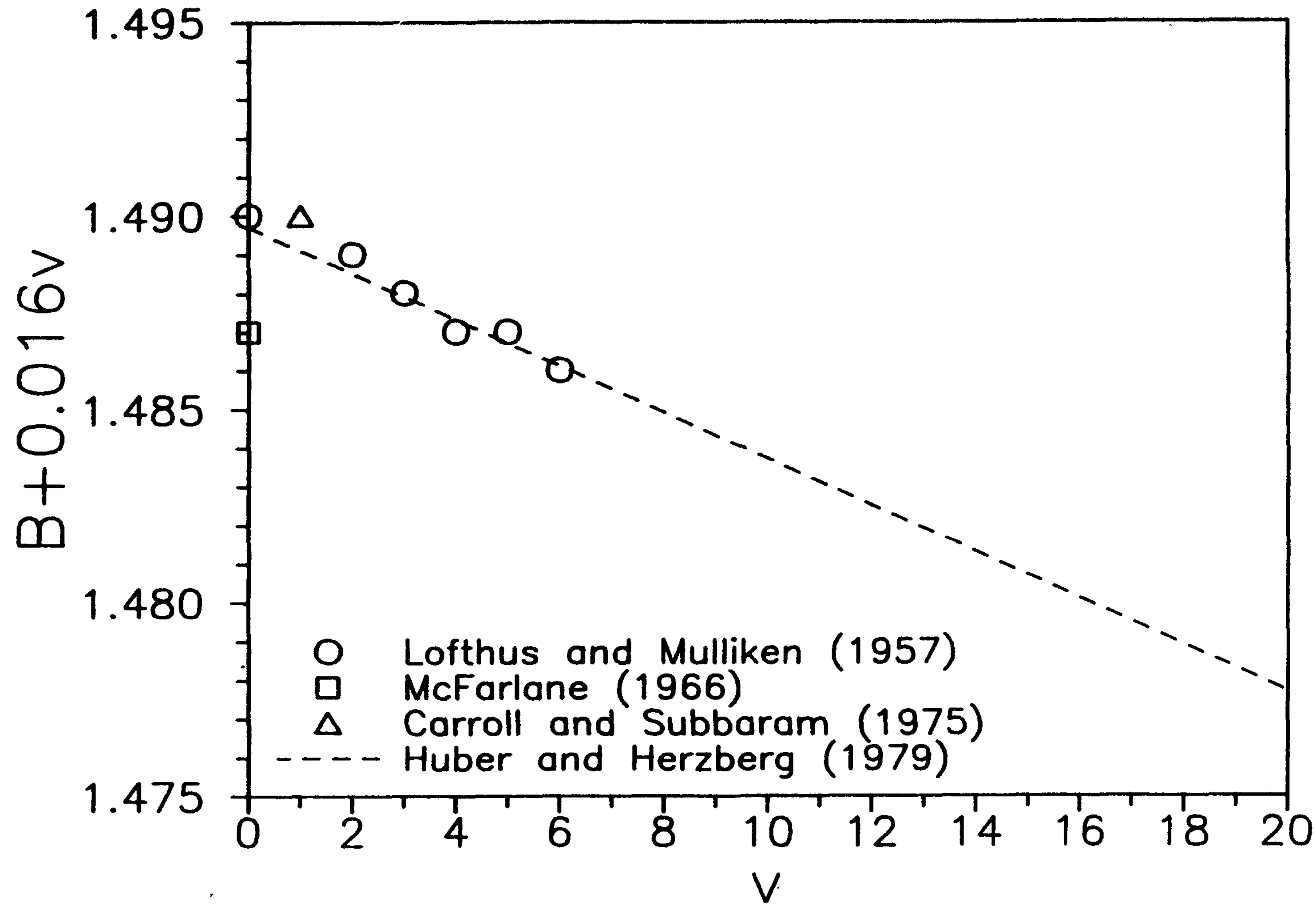

Figure 16. Rotational data and fit for the $w\ ^1\Delta_u$ state of N_2.

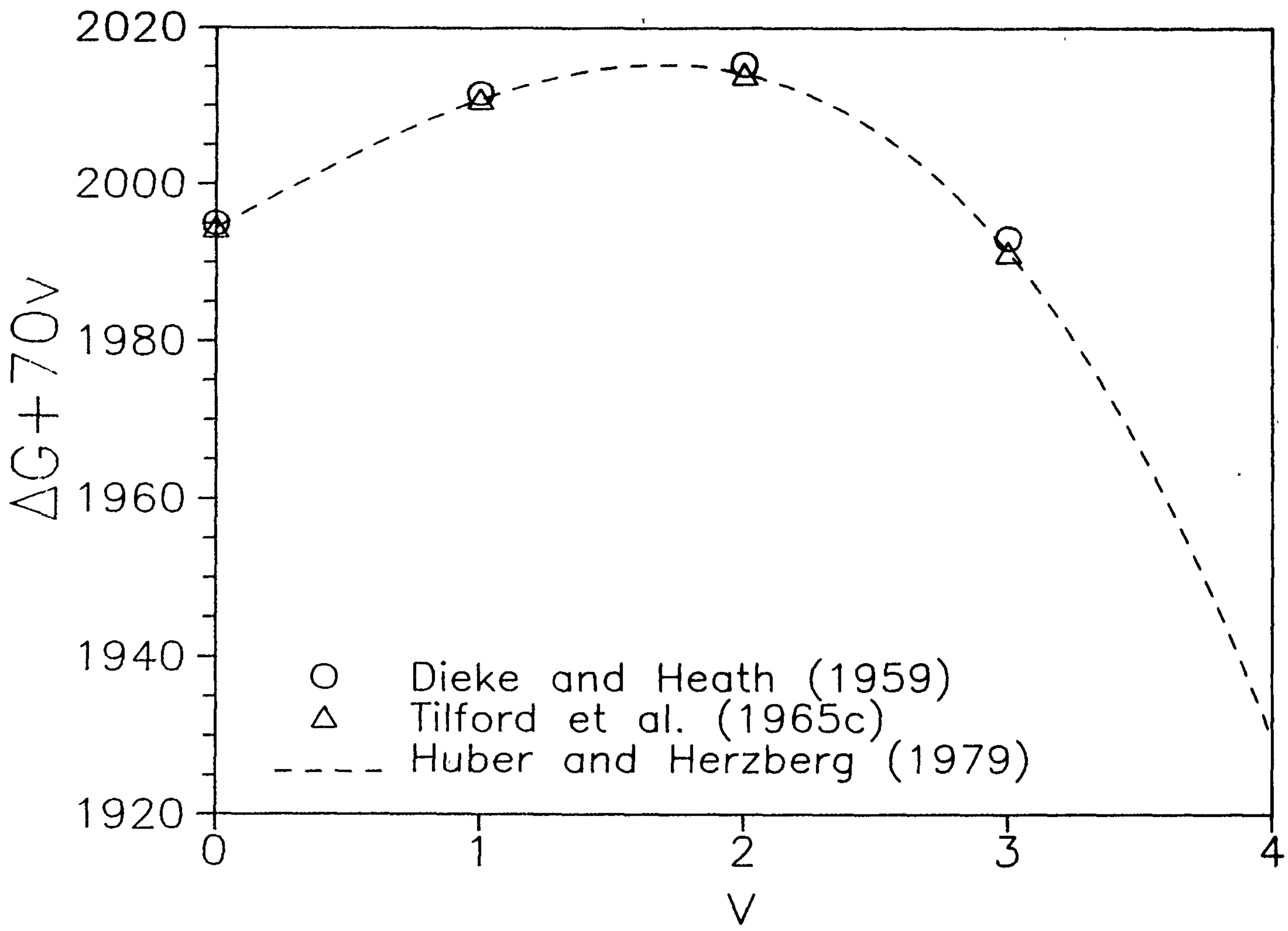

Figure 17. Vibrational data and fit for the $C\ {}^3\Pi_u$ state of N_2.

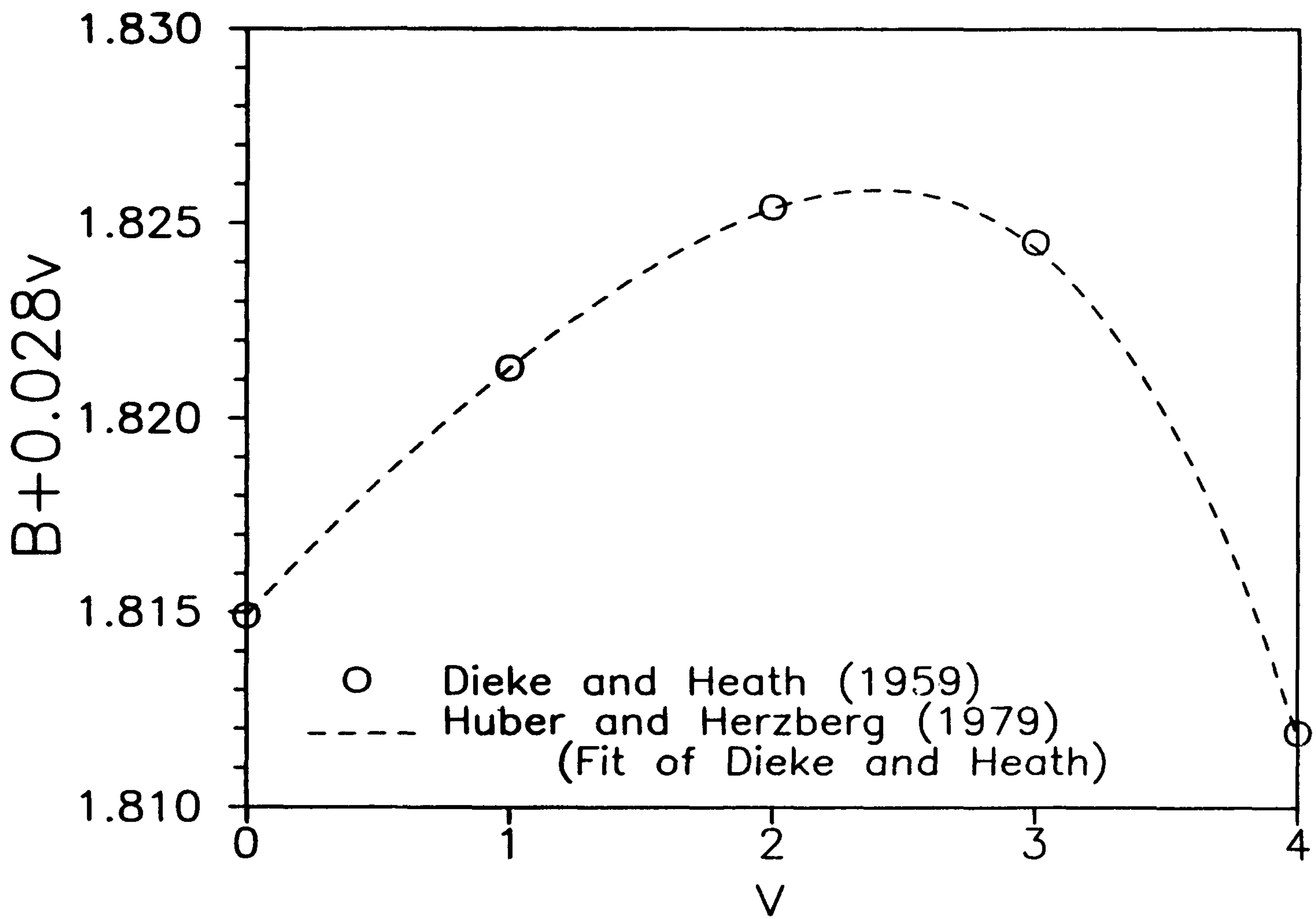

Figure 18. Rotational data and fit for the $C\ {}^3\Pi_u$ state of N_2.

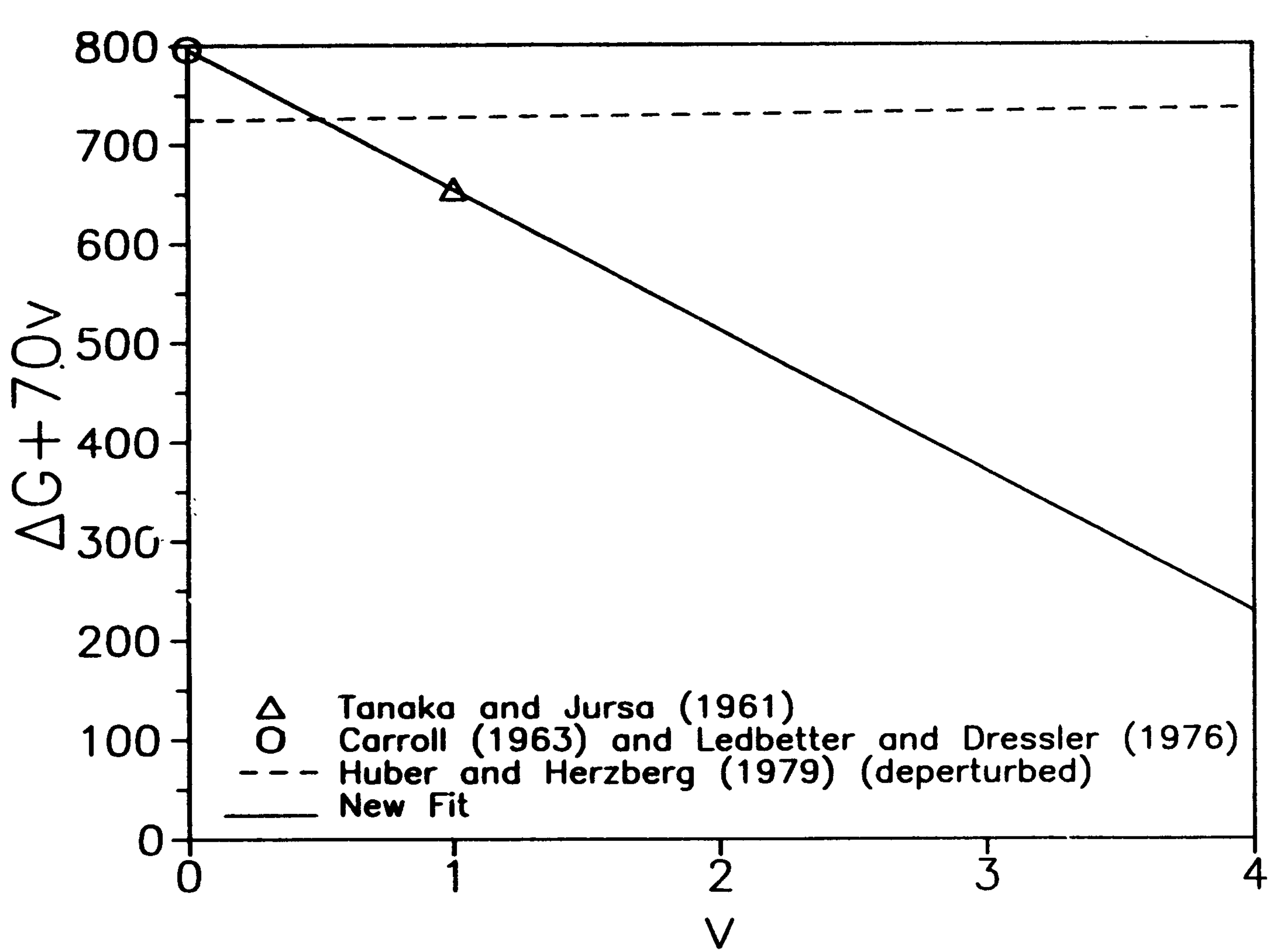

Figure 19. Vibrational data and fits for the $C'\ ^3\Pi_u$ state of N_2.

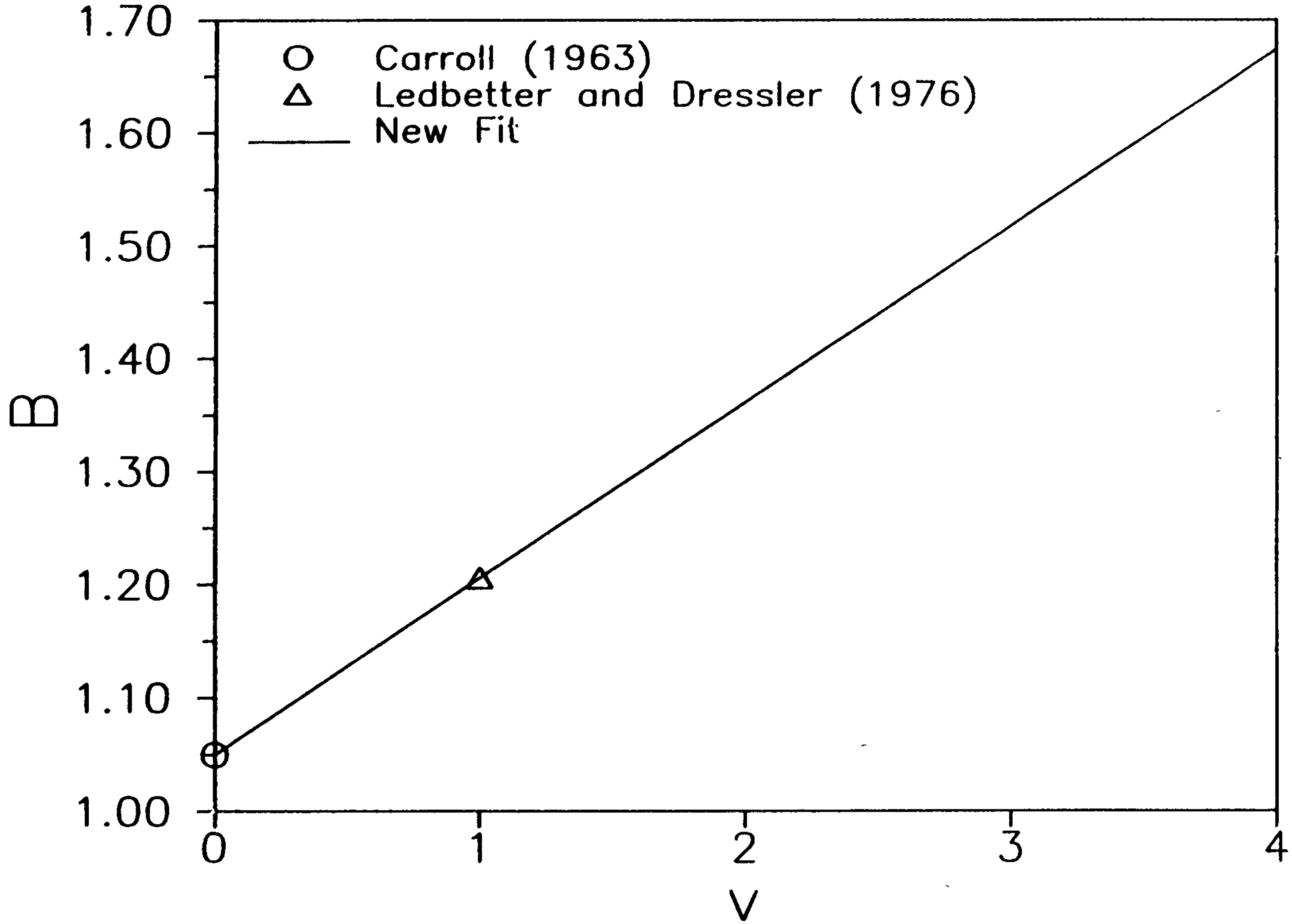

Figure 20. Rotational data and fit for the $C'\,^3\Pi_u$ state of N_2.

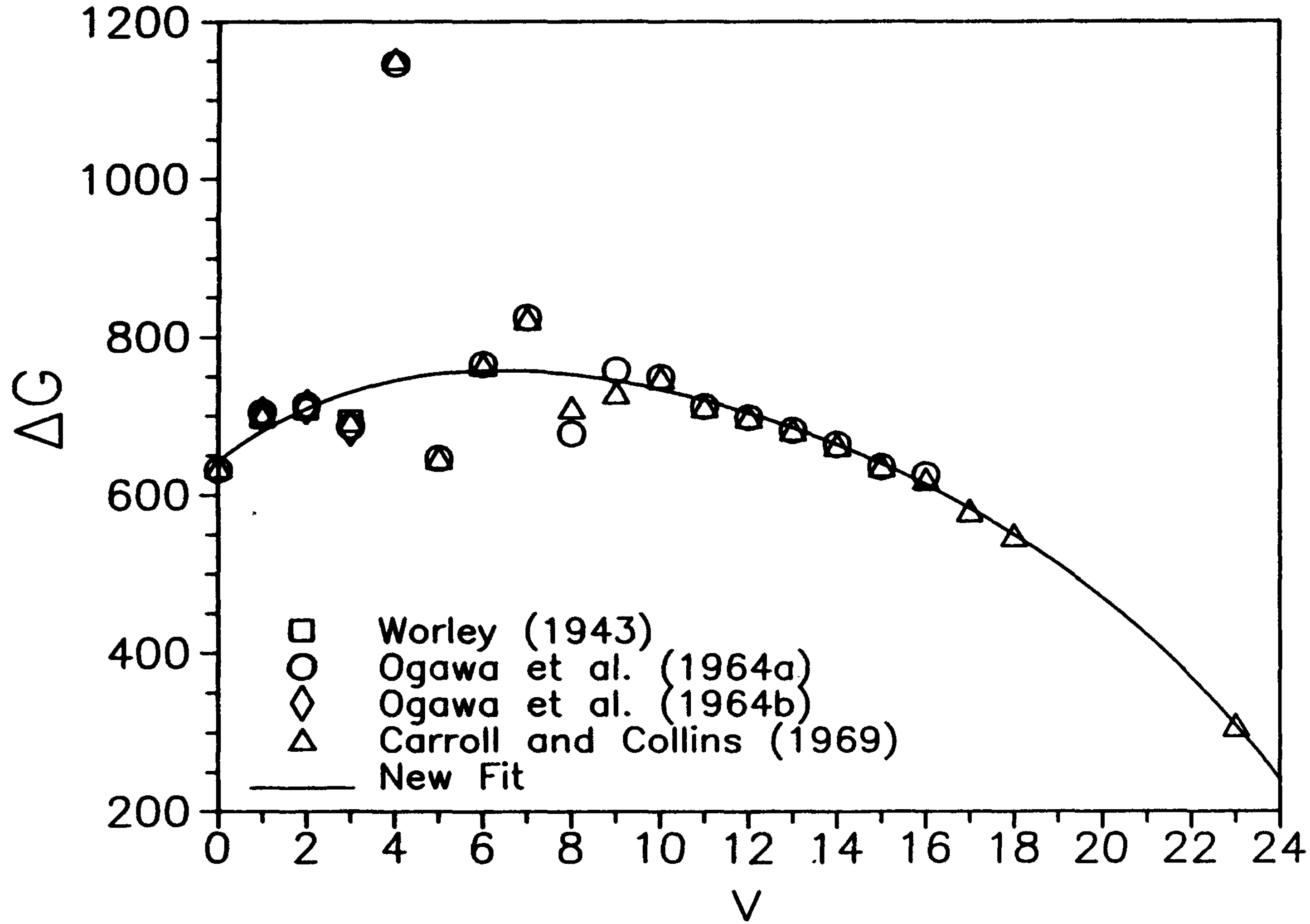

Figure 21. Vibrational data and fit for the $b\ ^1\Pi_u$ state of N_2.

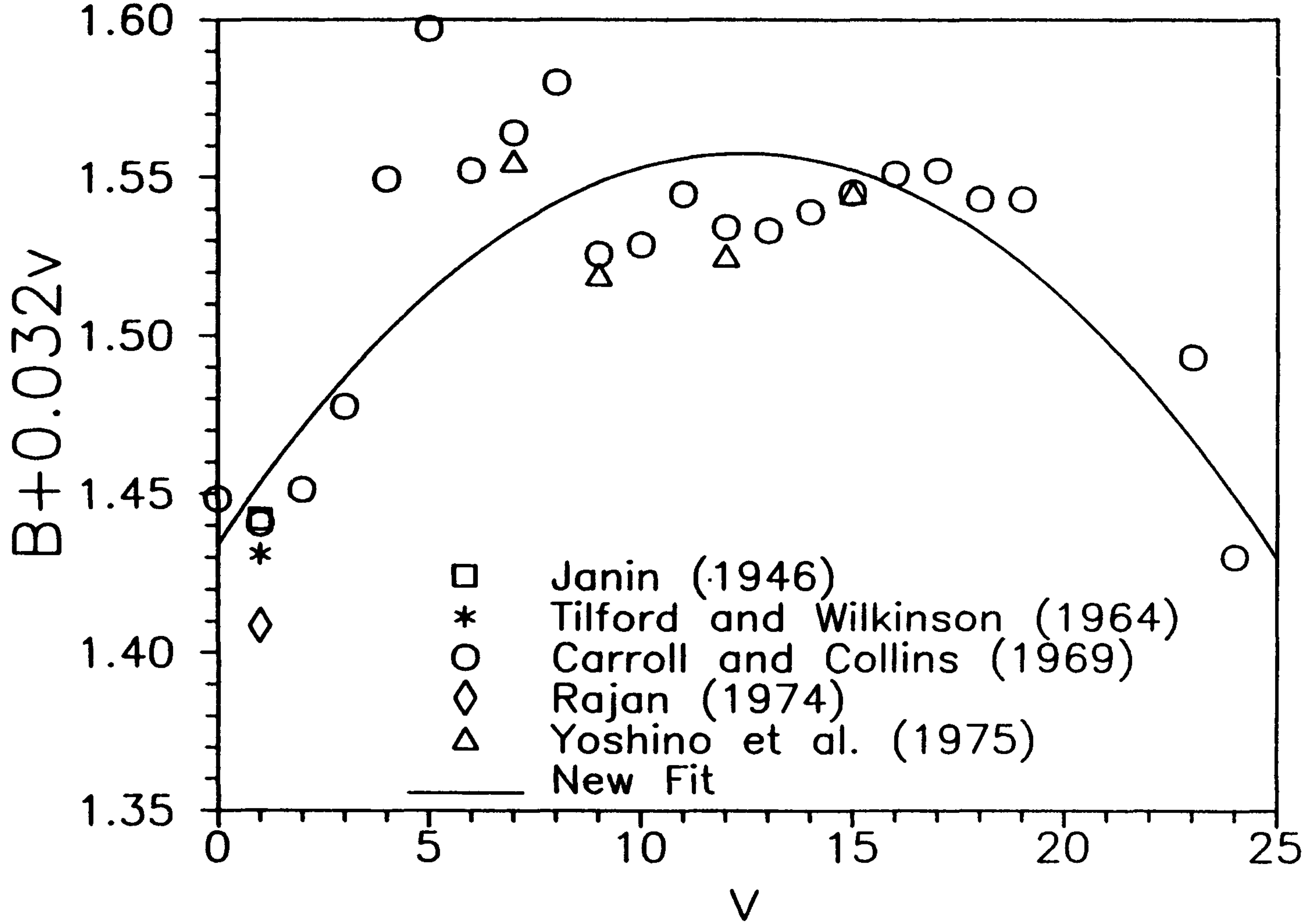

Figure 22. Rotational data and fit for the $b\ ^1\Pi_u$ state of N_2.

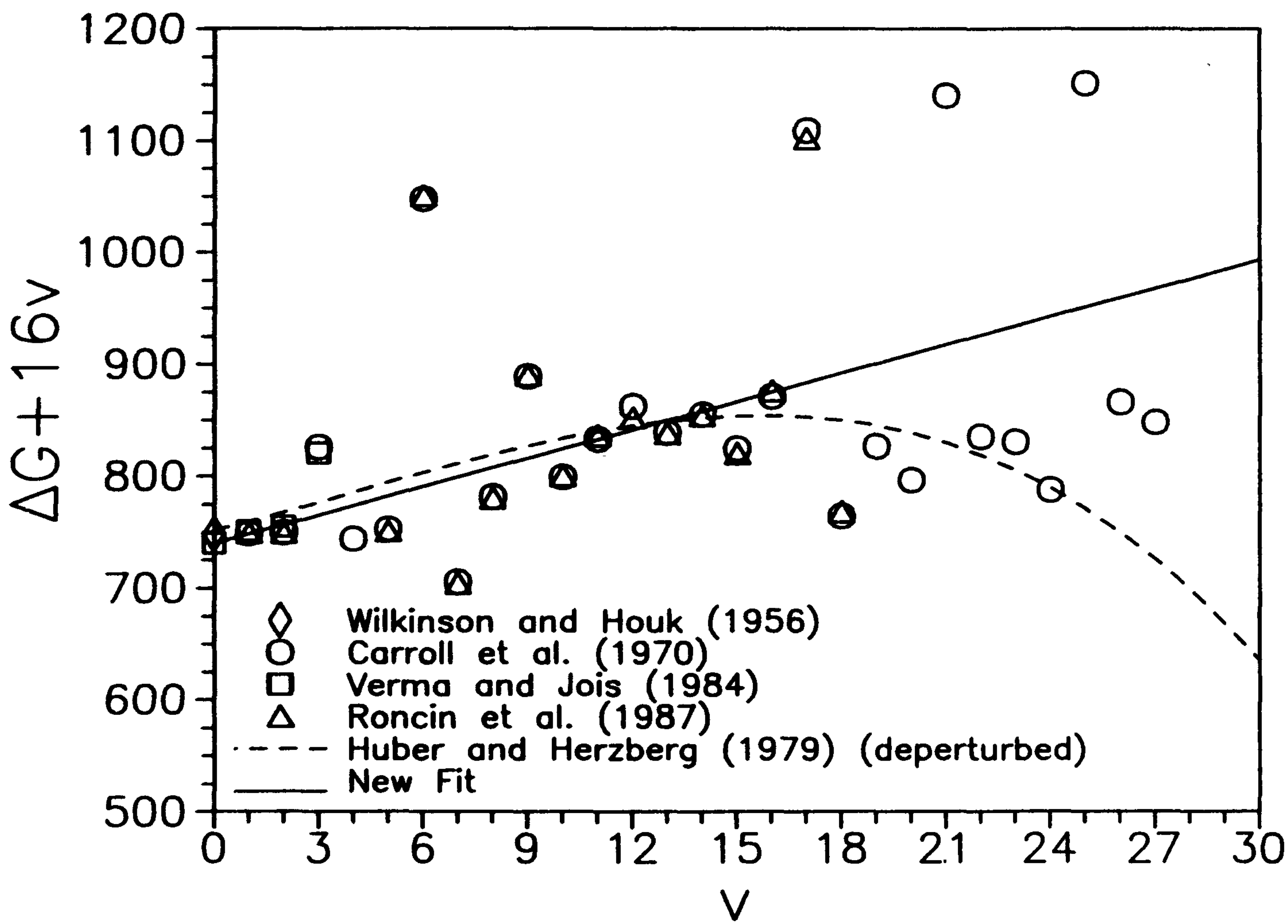

Figure 23. Vibrational data and fits for the $b'\ ^1\Sigma_u^+$ state of N_2.

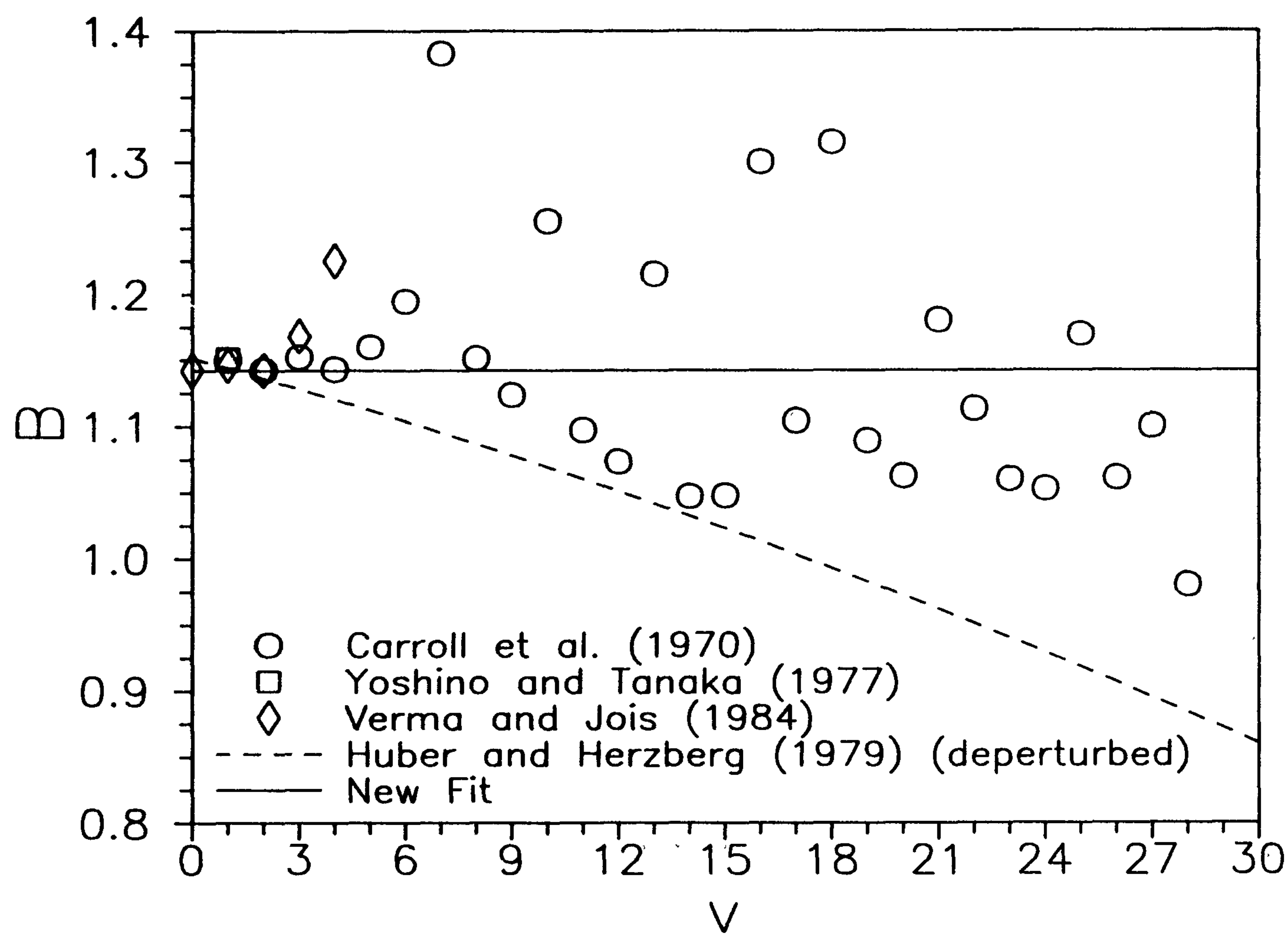

Figure 24. Rotational data and fits for the $b'\ {}^1\Sigma_u^+$ state of N_2.

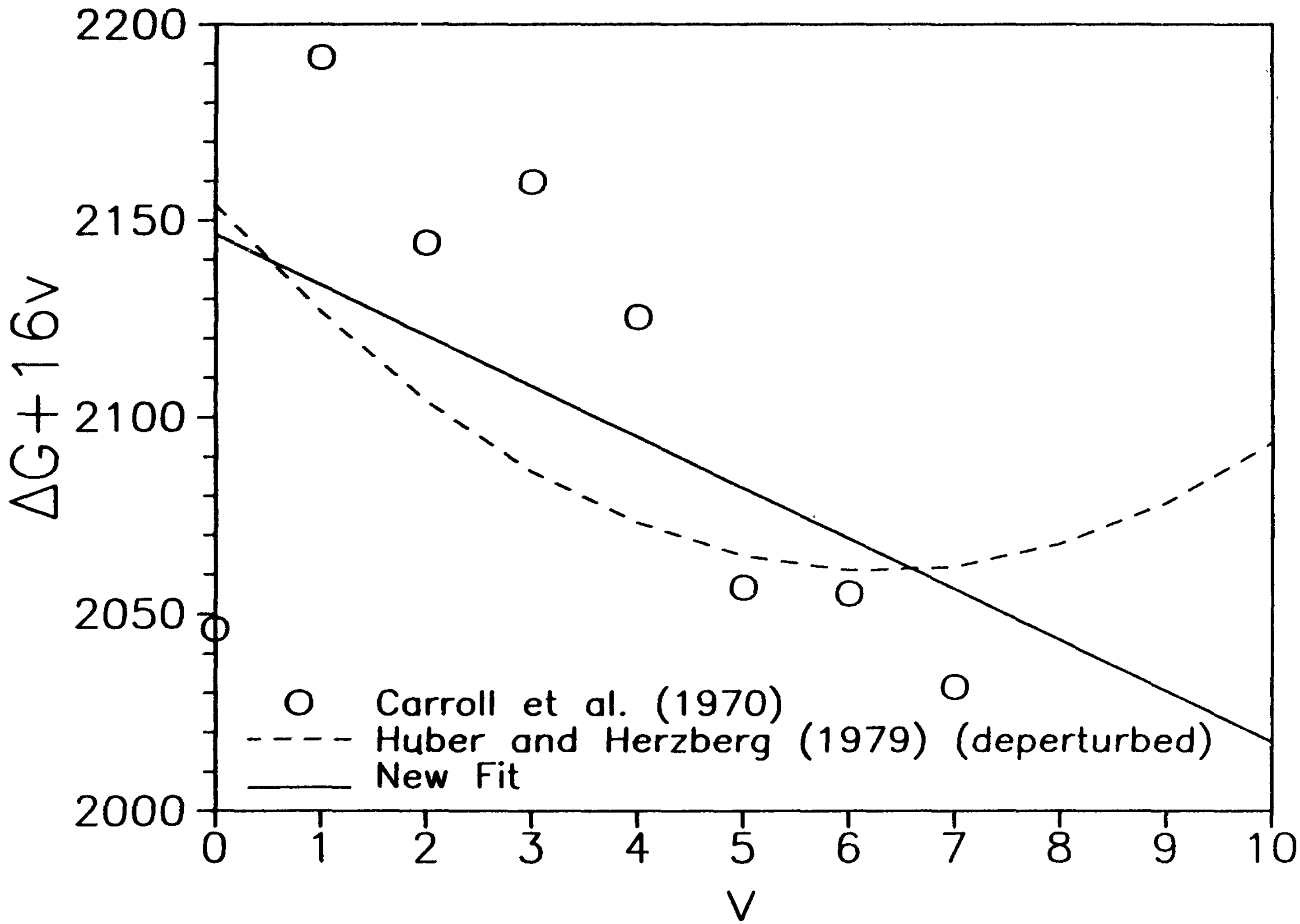

Figure 25. Vibrational data and fits for the $c_4'\ {}^1\Sigma_u^+$ state of N_2.

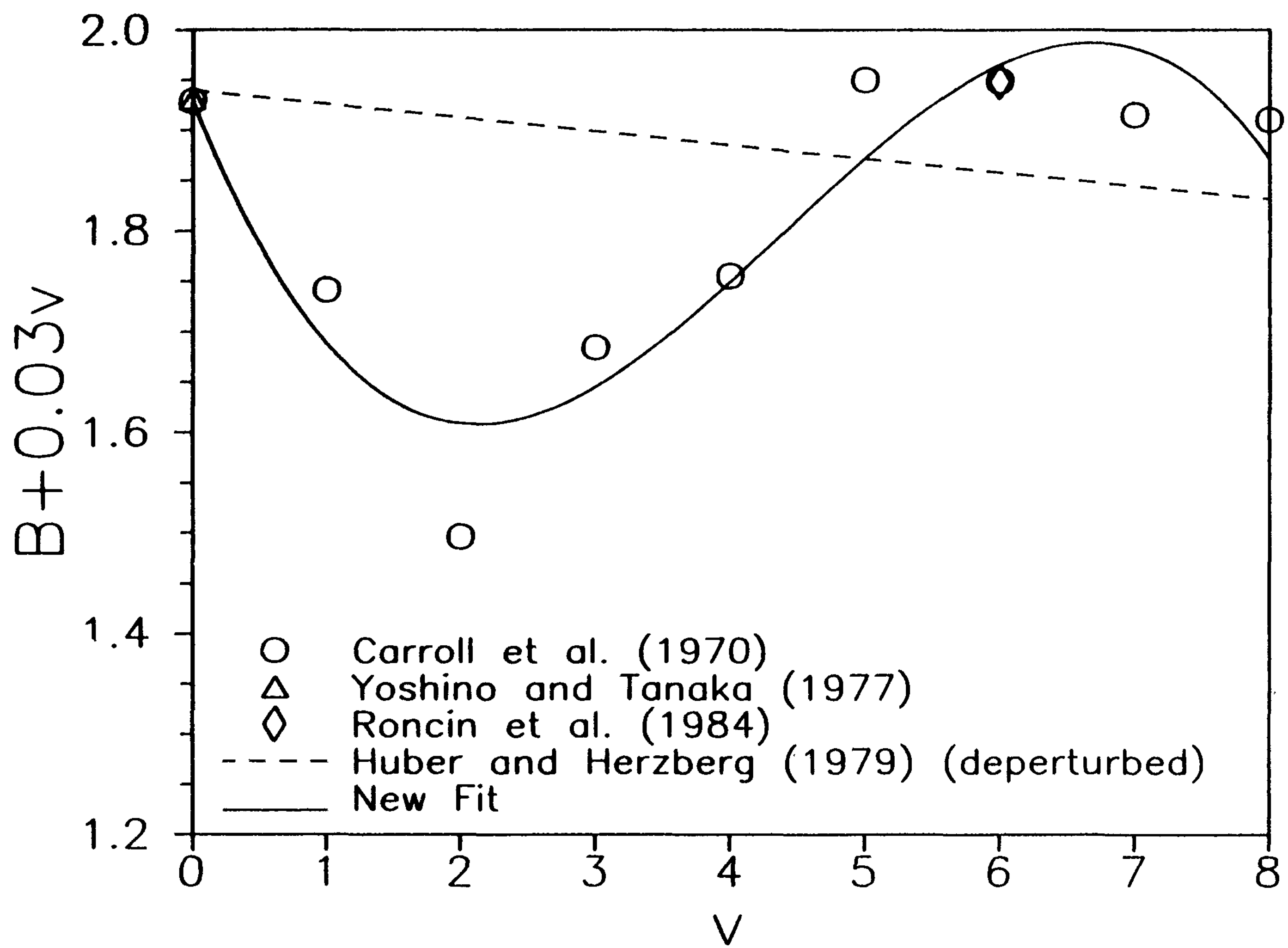

Figure 26. Rotational data and fits for the $c_4' \, ^1\Sigma_u^+$ state of N_2.

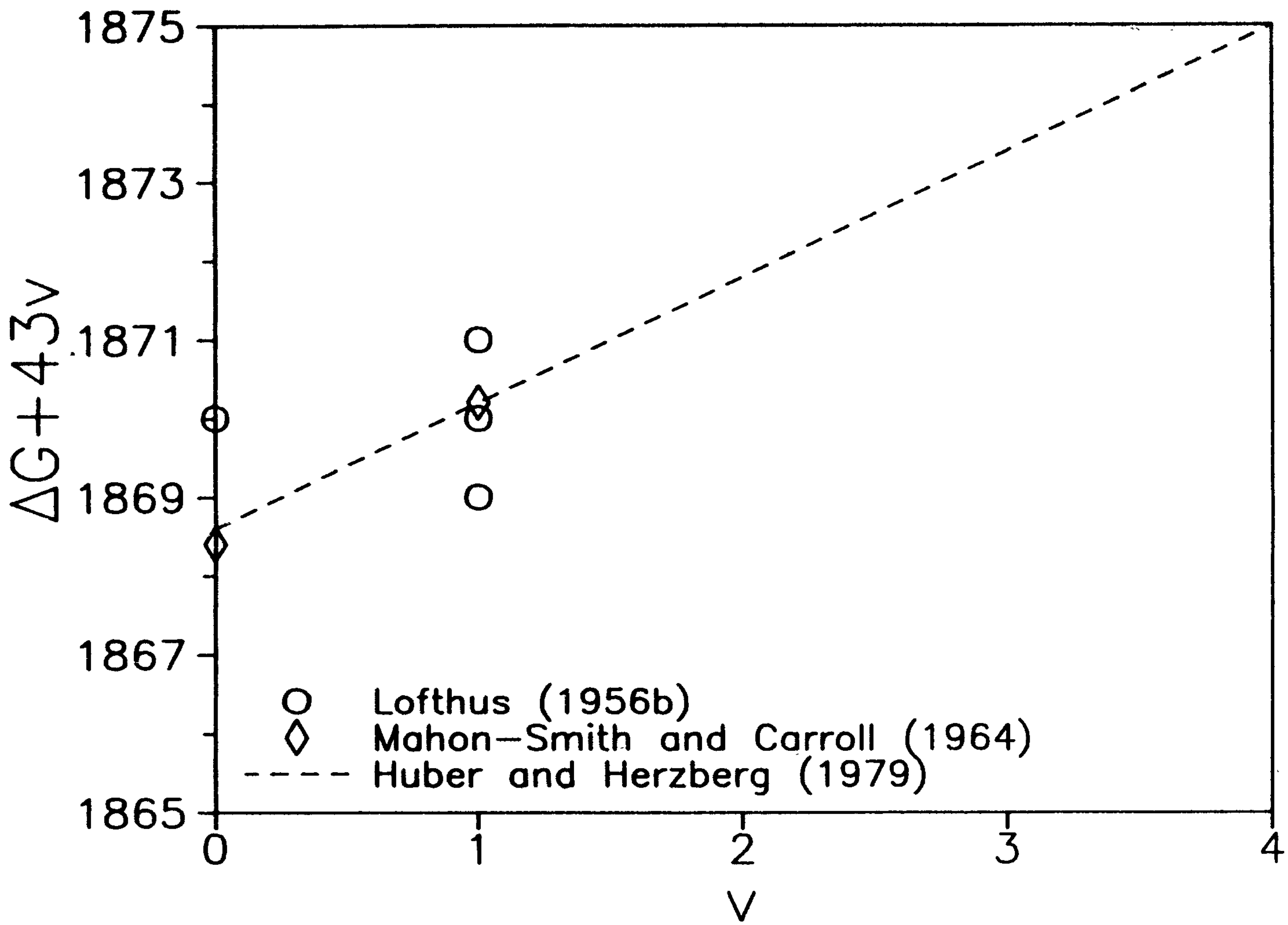

Figure 27. Vibrational data and fit for the $x\ ^1\Sigma_g^-$ state of N_2.

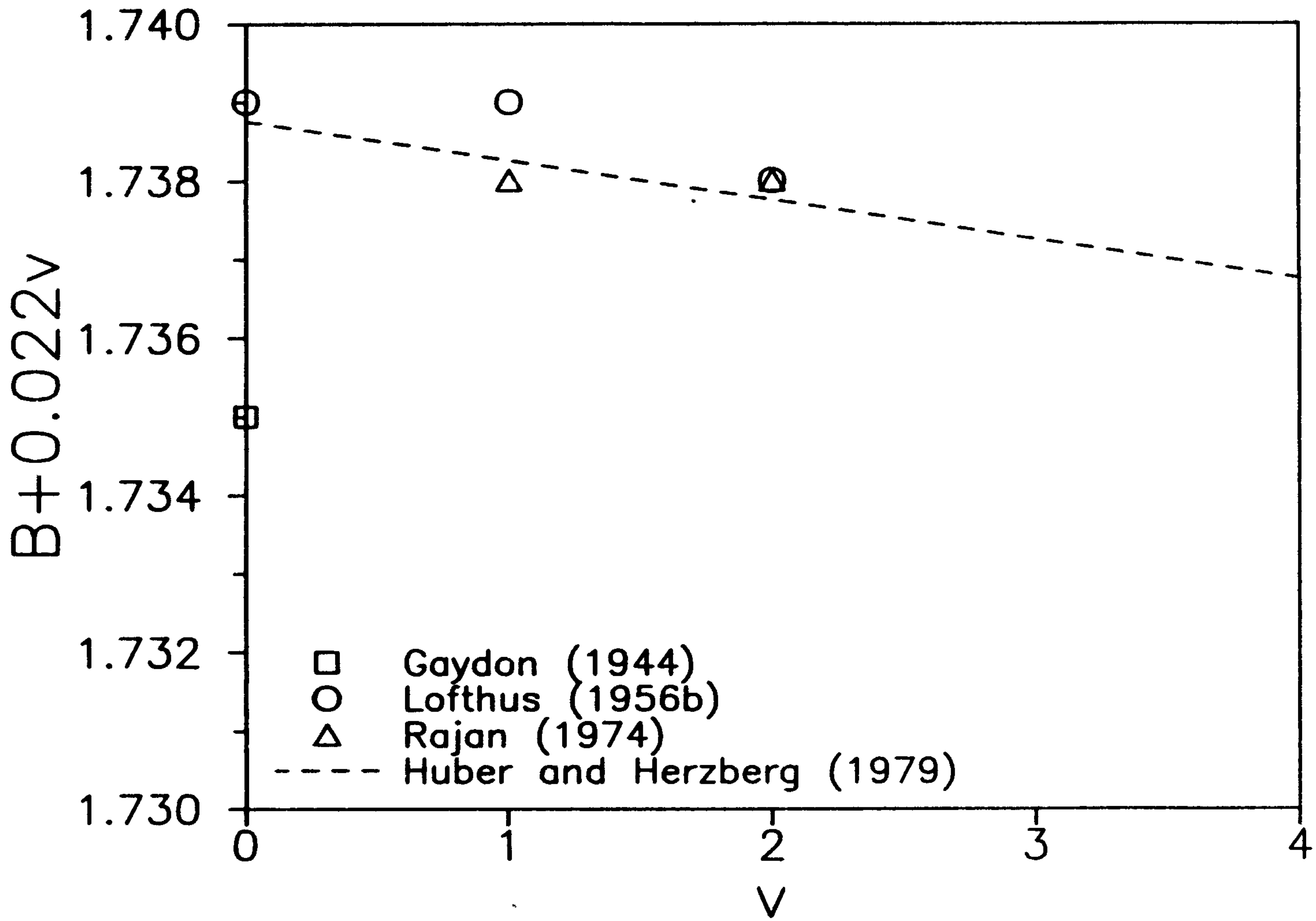

Figure 28. Rotational data and fit for the $x\ ^1\Sigma_g^-$ state of N_2.

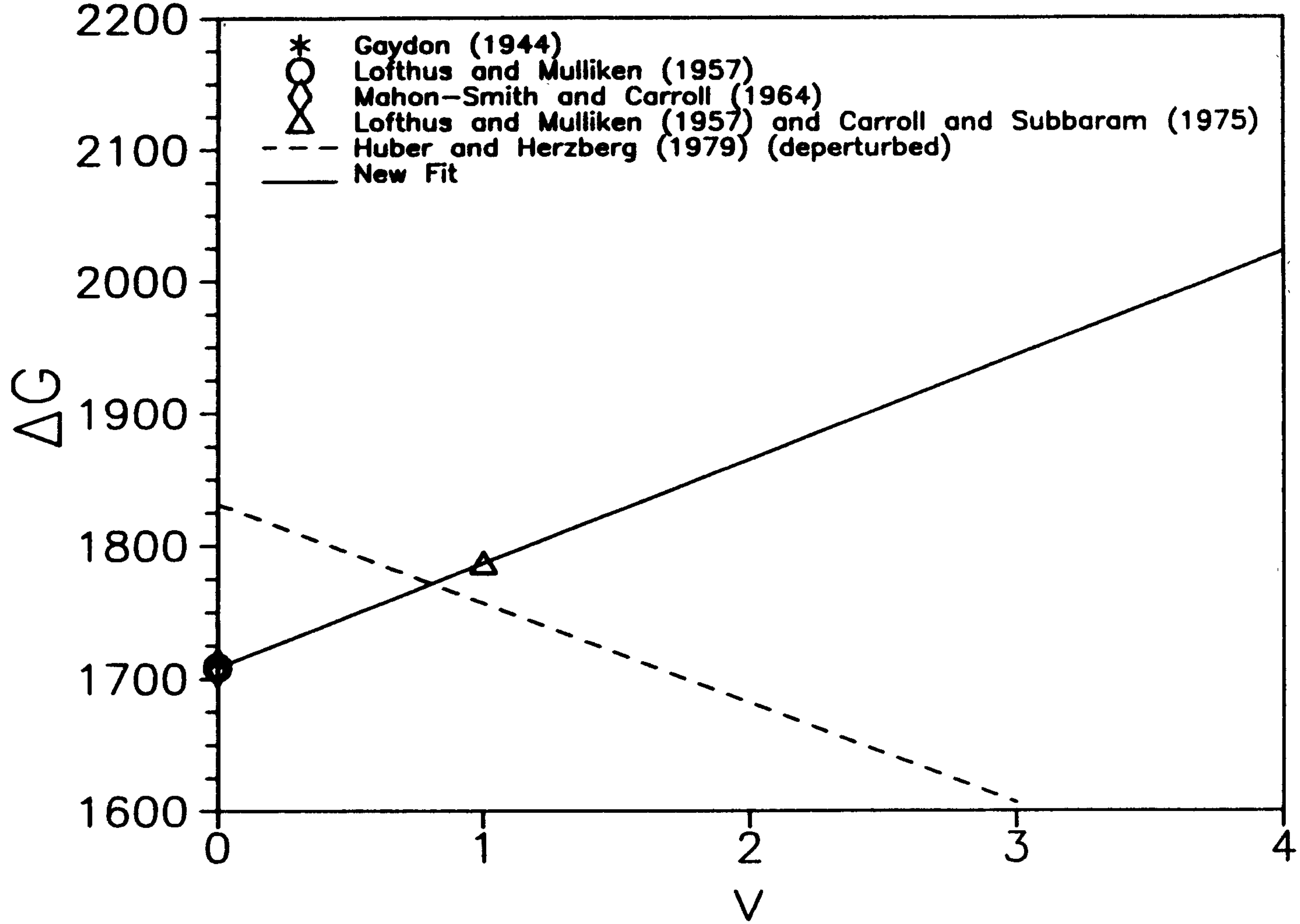

Figure 29. Vibrational data and fits for the $y\ ^1\Pi_g$ state of N_2.

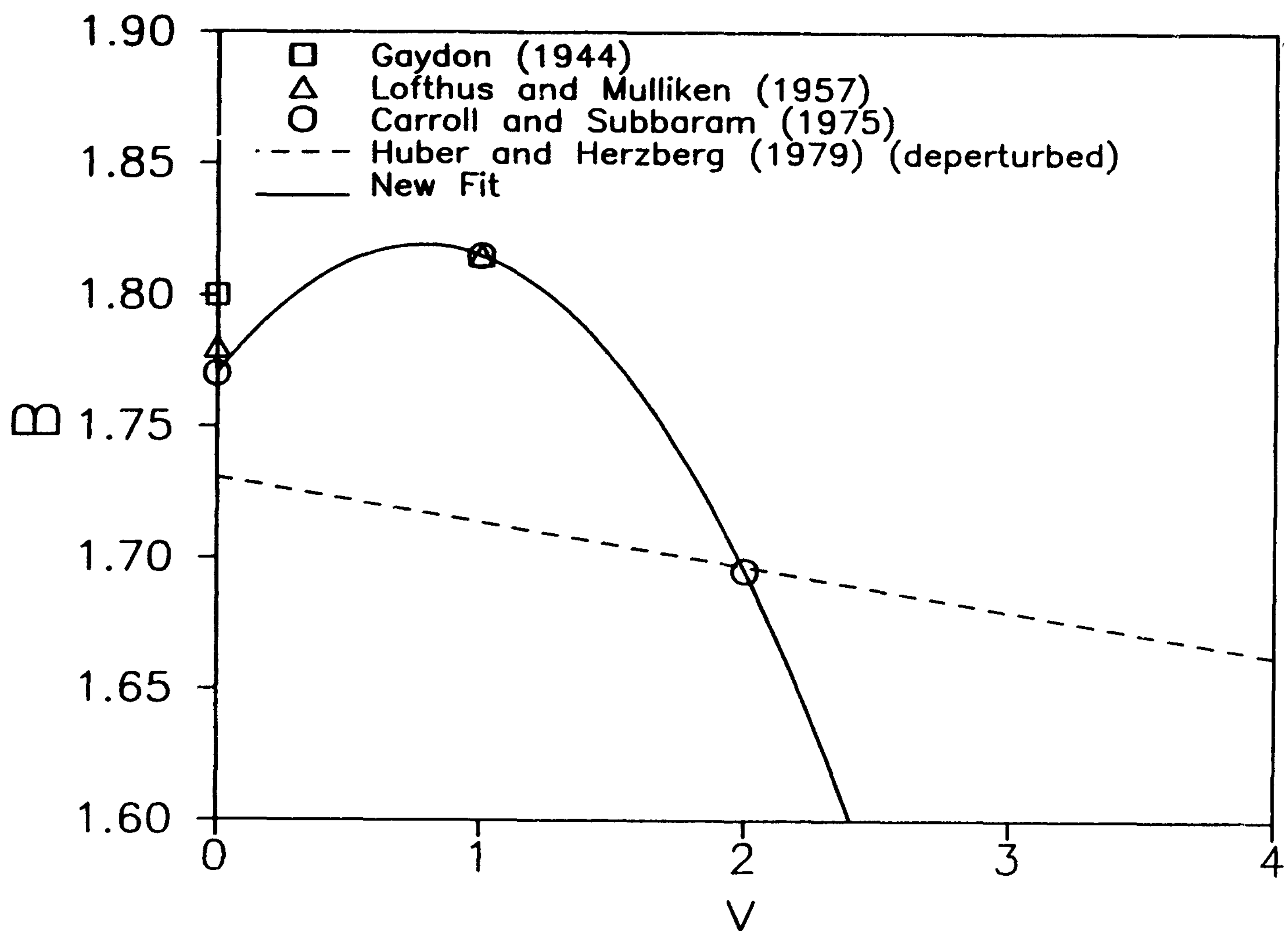

Figure 30. Rotational data and fits for the $y\ ^1\Pi_g$ state of N_2.

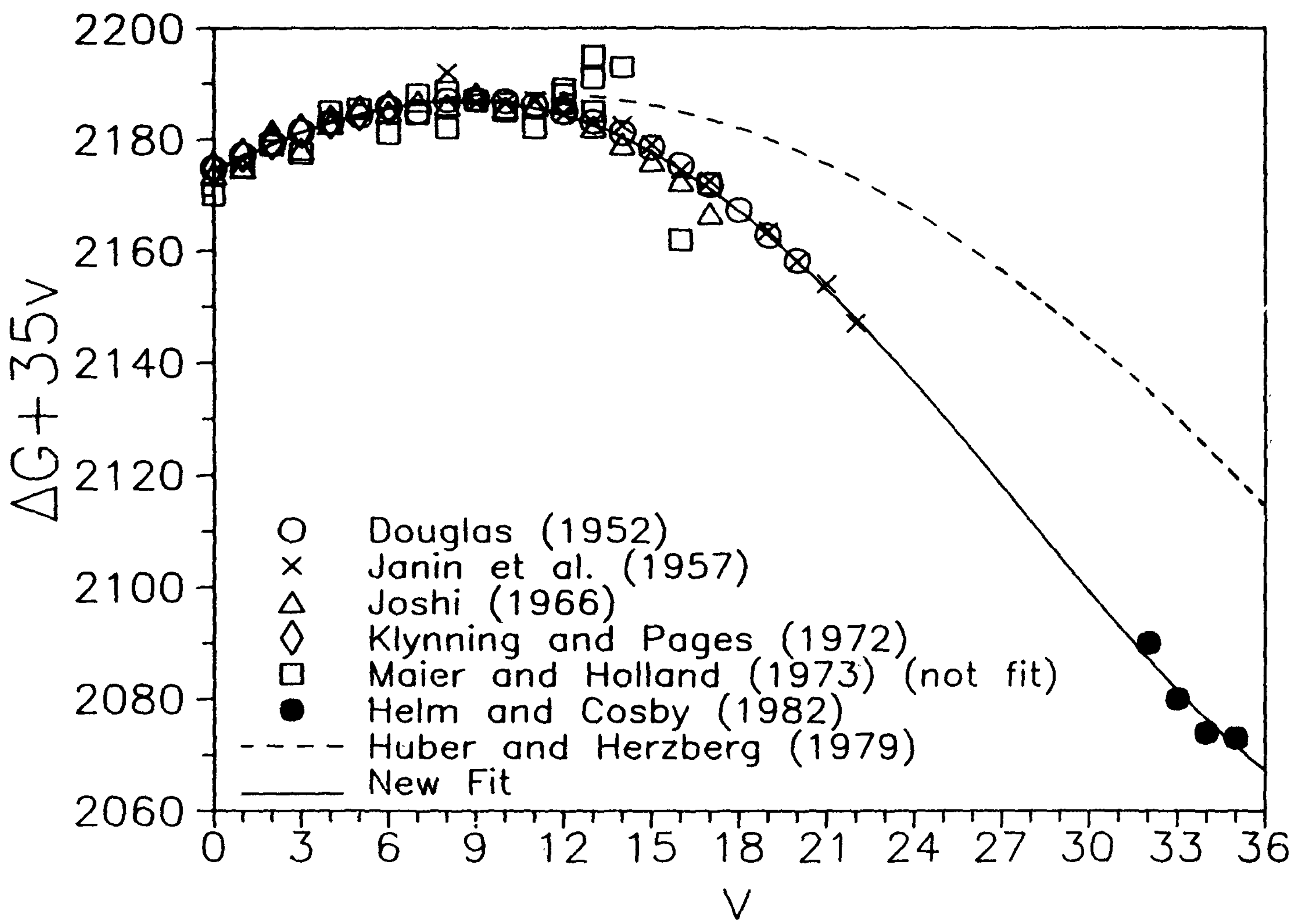

Figure 31. Vibrational data and fits for the $X\ ^2\Sigma_g^+$ state of N_2^+.

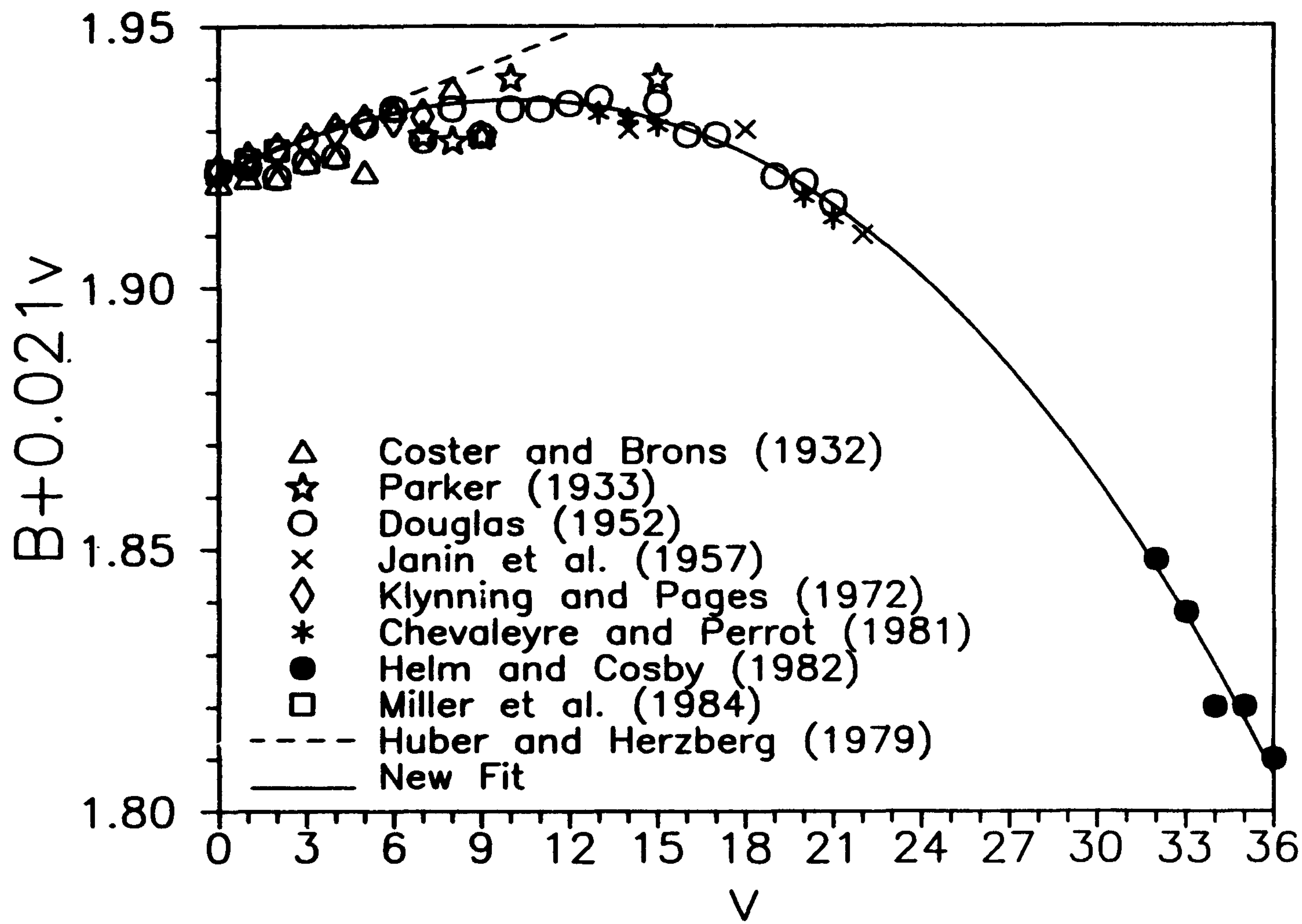

Figure 32. Rotational data and fits for the $X\ ^2\Sigma_g^+$ state of N_2^+.

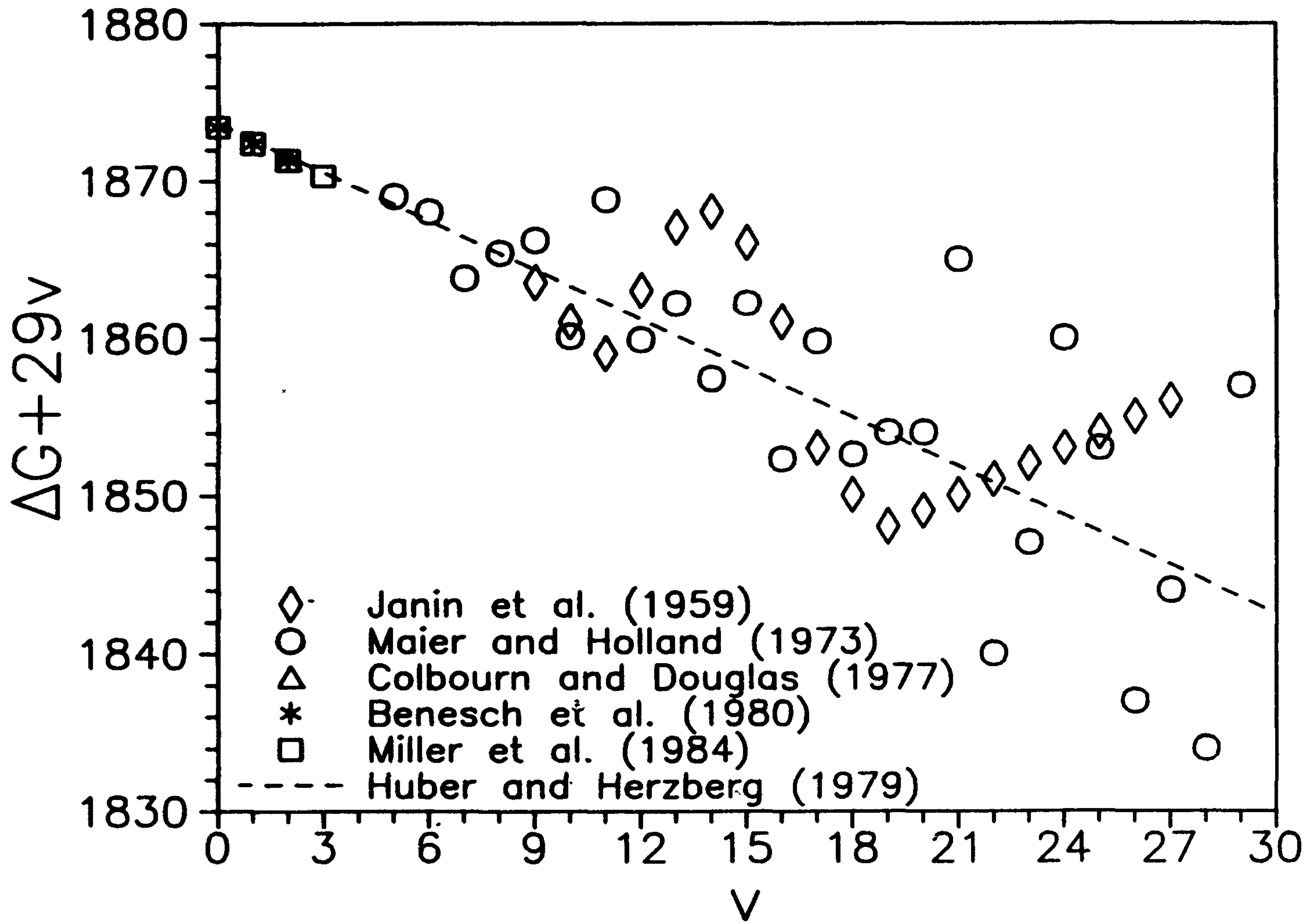

Figure 33. Vibrational data and fit for the $A\ ^2\Pi_u$ state of N_2^+.

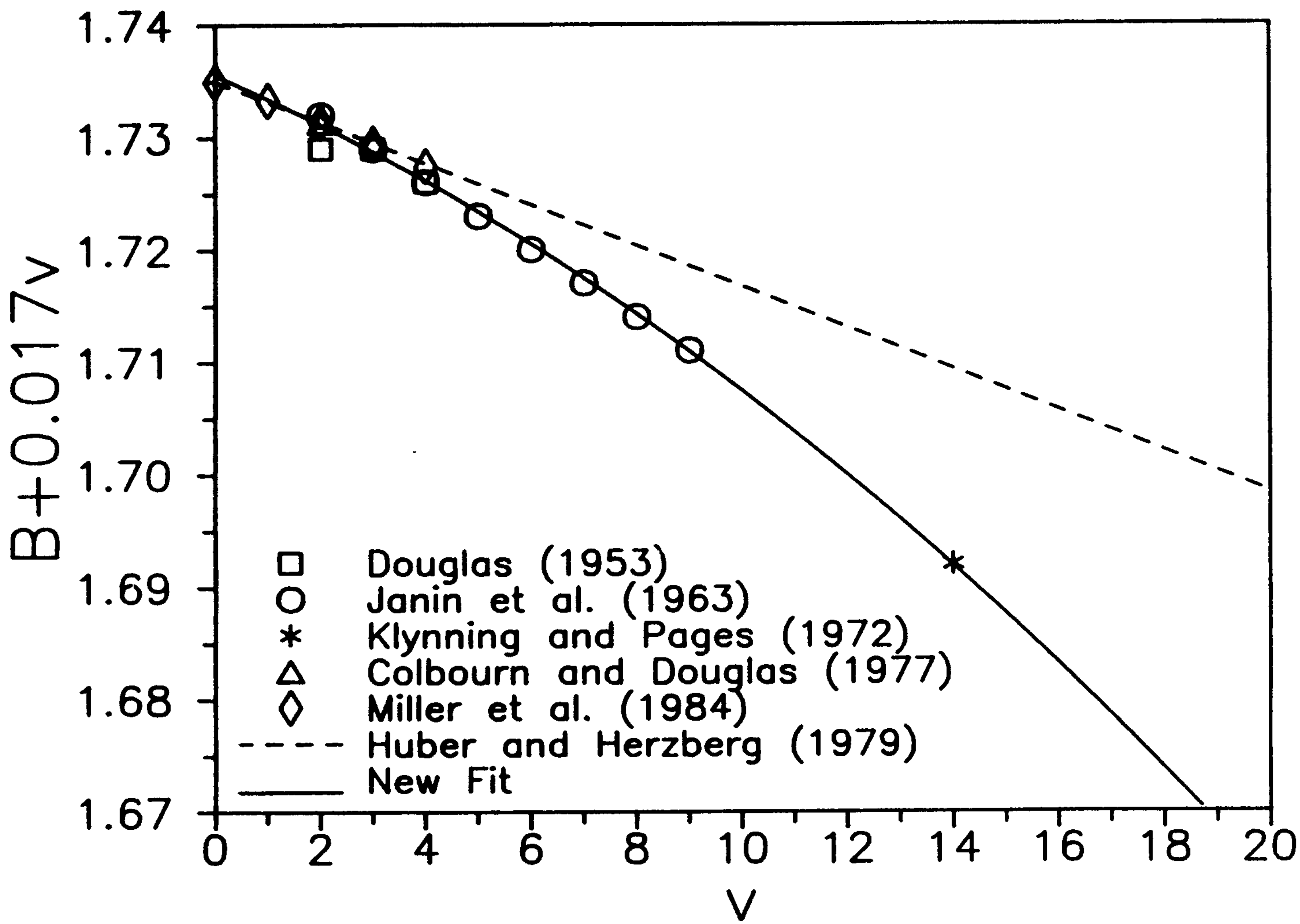

Figure 34. Rotational data and fits for the $A\ ^2\Pi_u$ state of N_2^+.

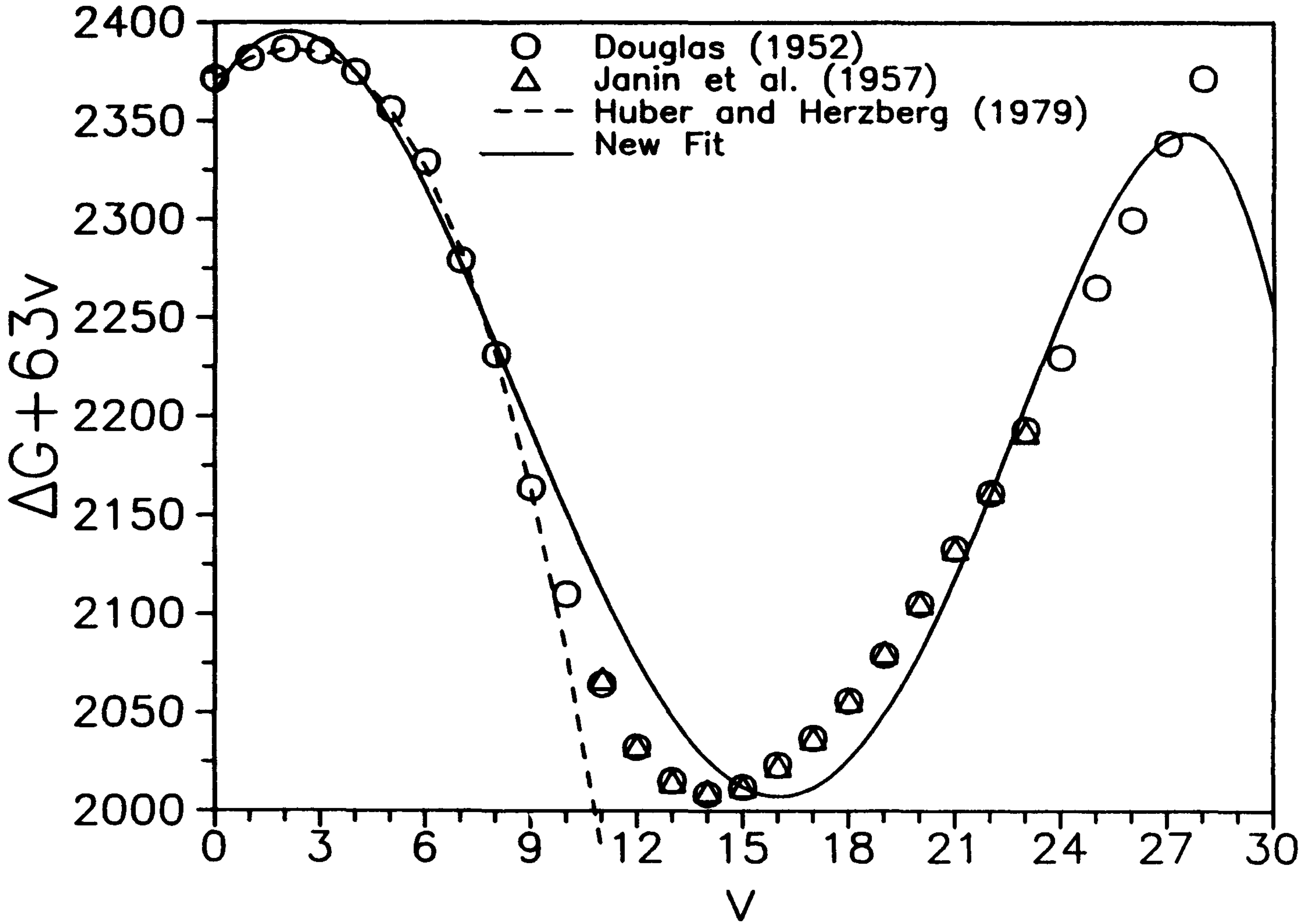

Figure 35. Vibrational data and fits for the $B\ ^2\Sigma_u^+$ state of N_2^+.

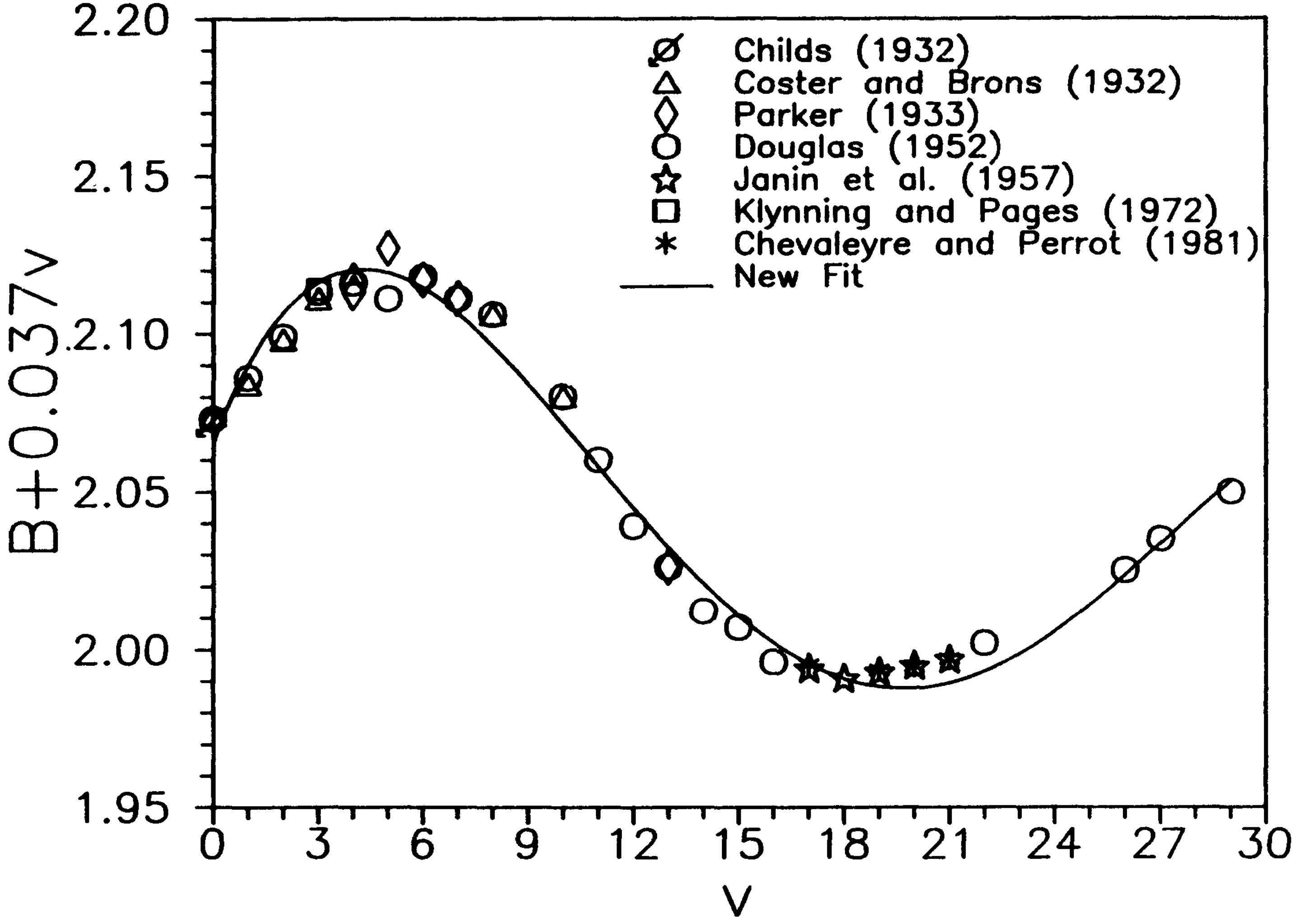

Figure 36. Rotational data and fit for the $B\ ^2\Sigma_u^+$ state of N_2^+.

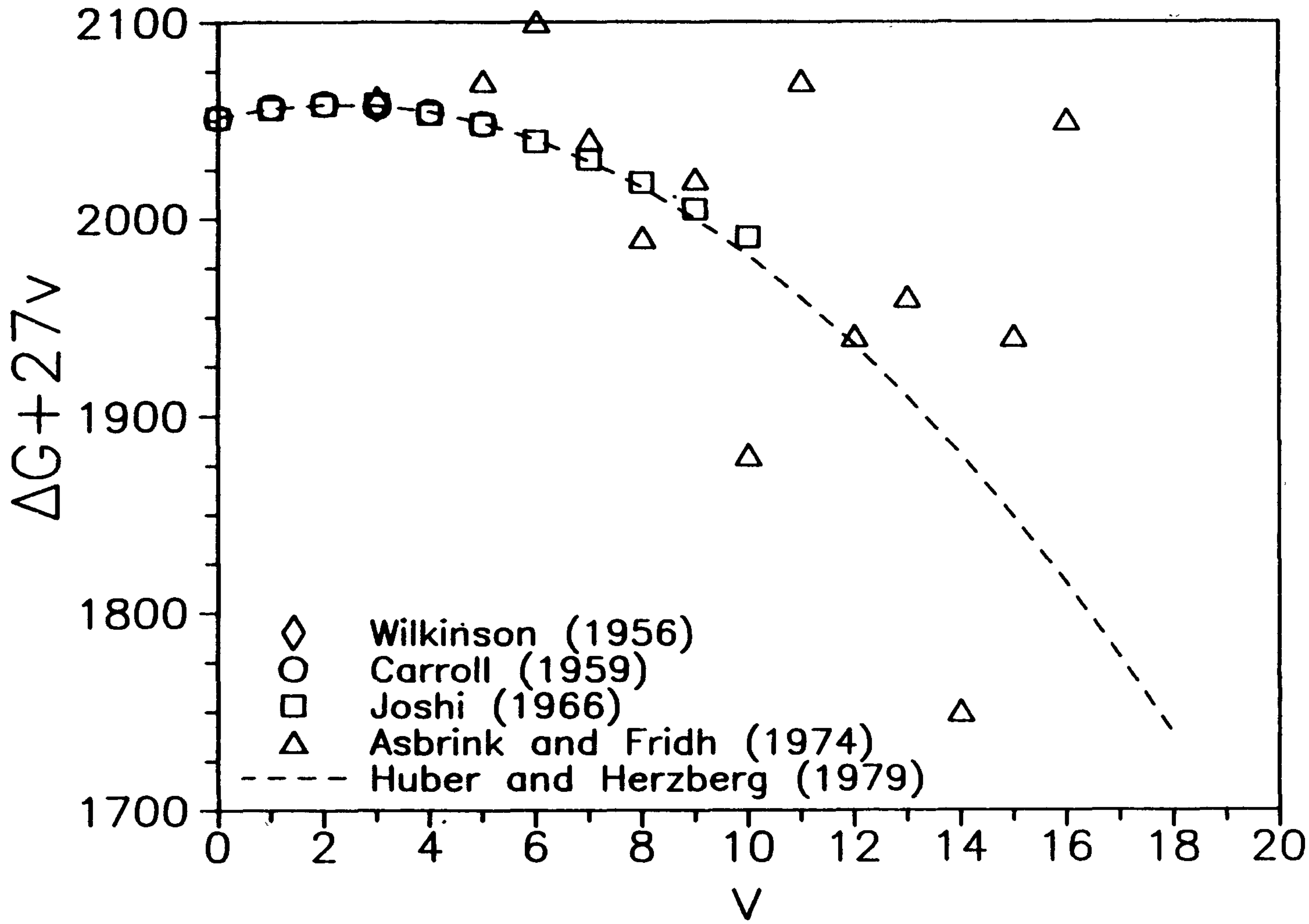

Figure 37. Vibrational data and fit for the $C\ ^2\Sigma_u^+$ state of N_2^+.

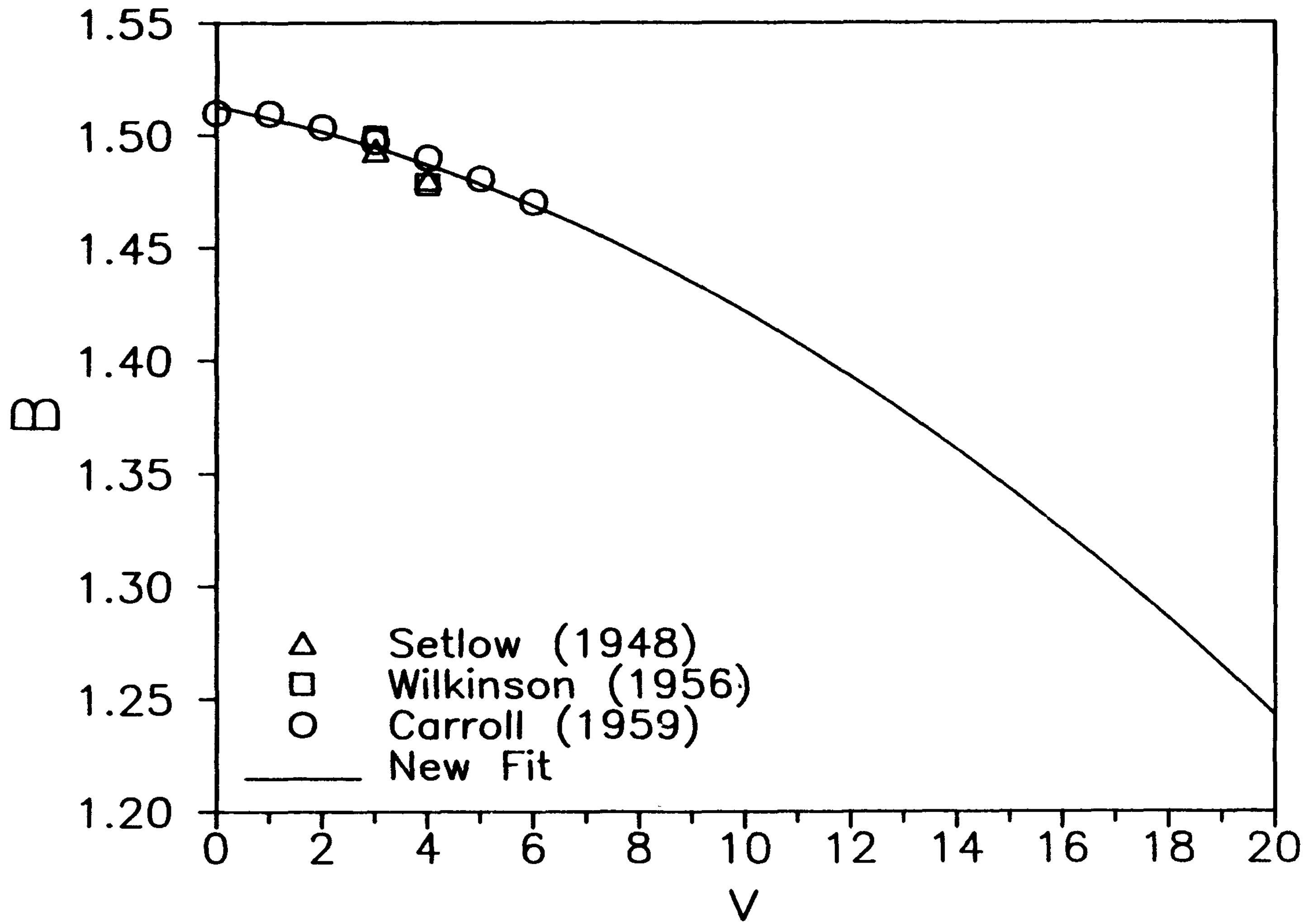

Figure 38. Rotational data and fit for the $C\ ^2\Sigma_u^+$ state of N_2^+.

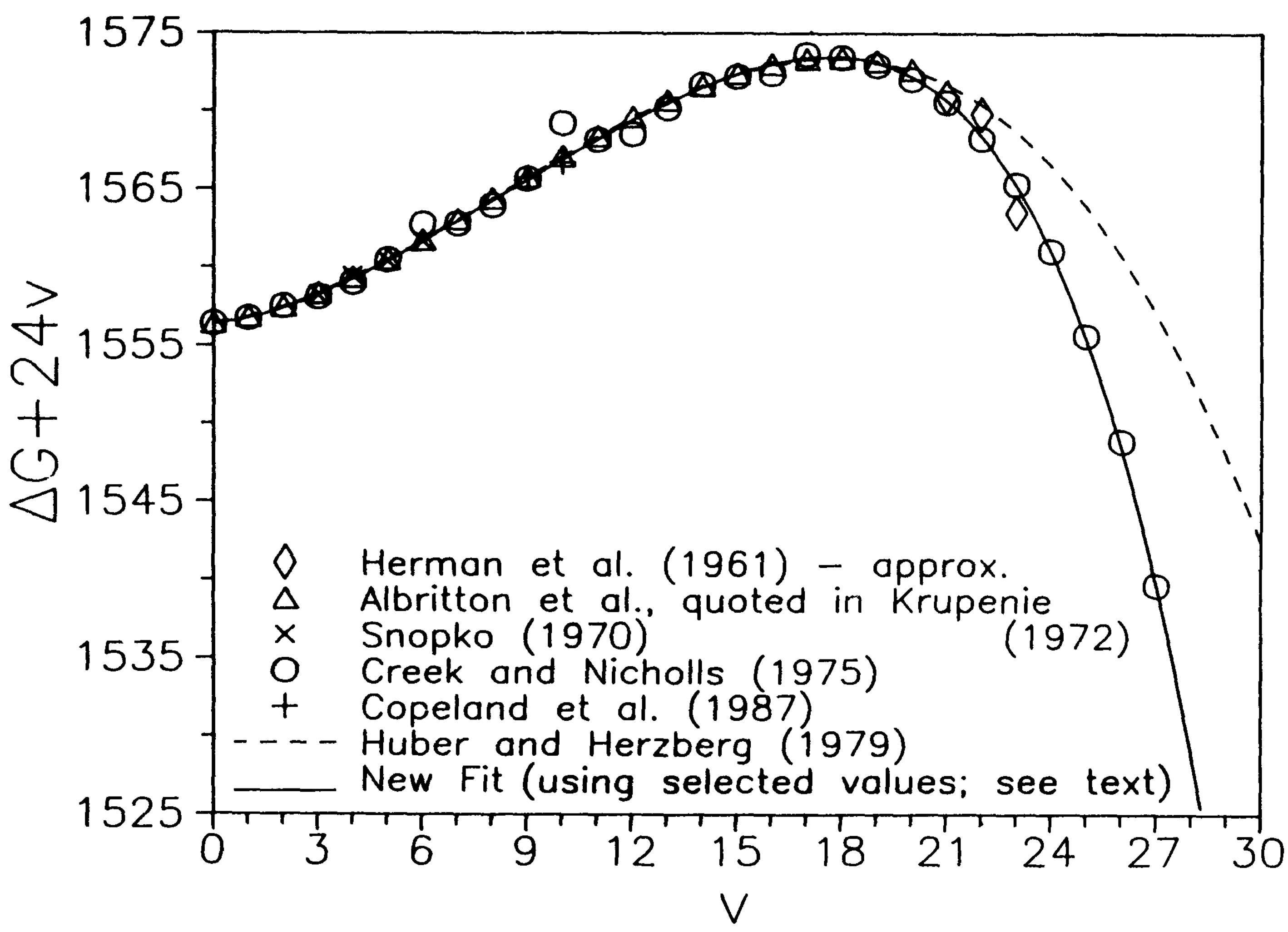

Figure 39. Vibrational data and fits for the $X\ ^3\Sigma_g^-$ state of O_2.

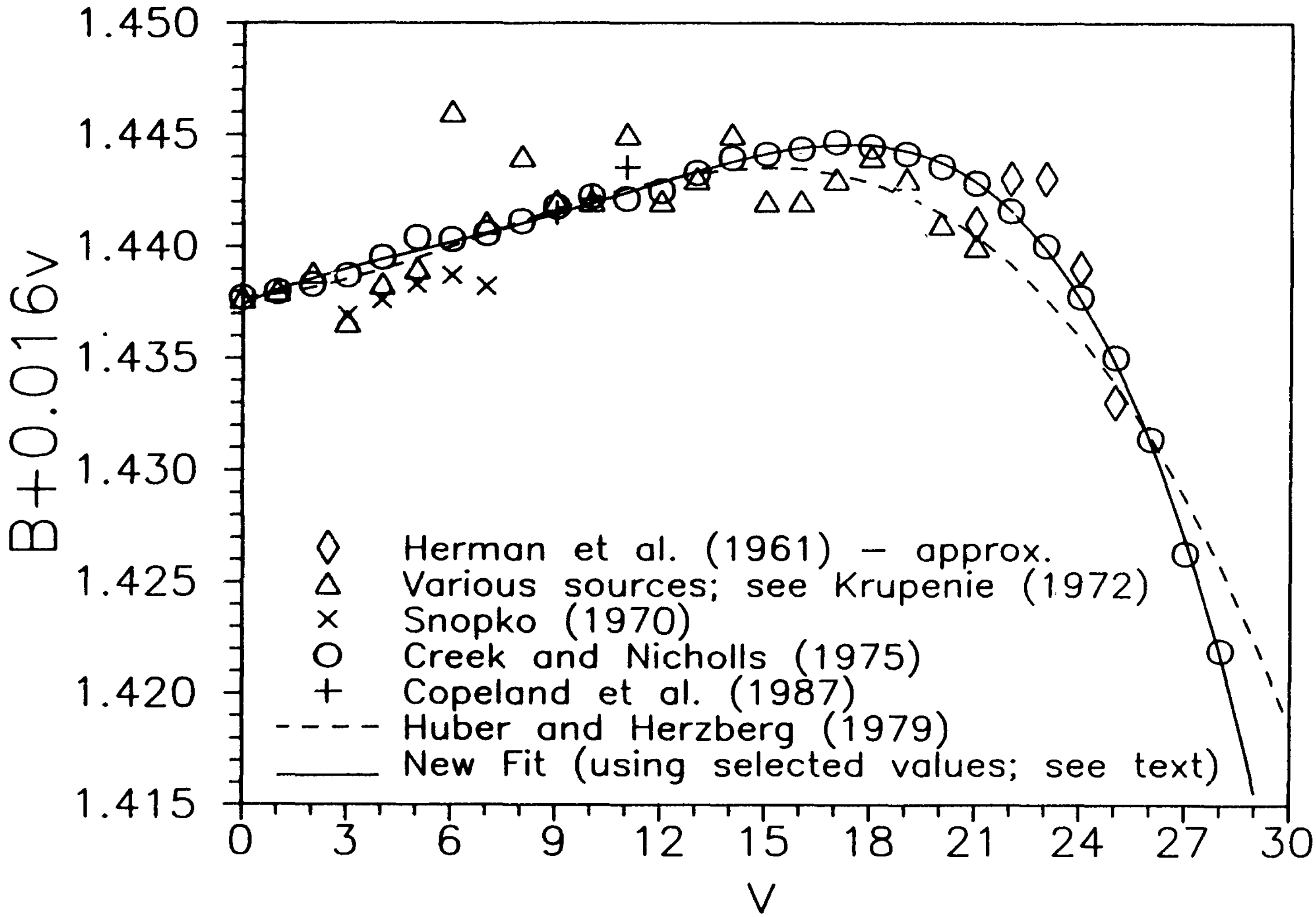

Figure 40. Rotational data and fits for the $X\ ^3\Sigma_g^-$ state of O_2.

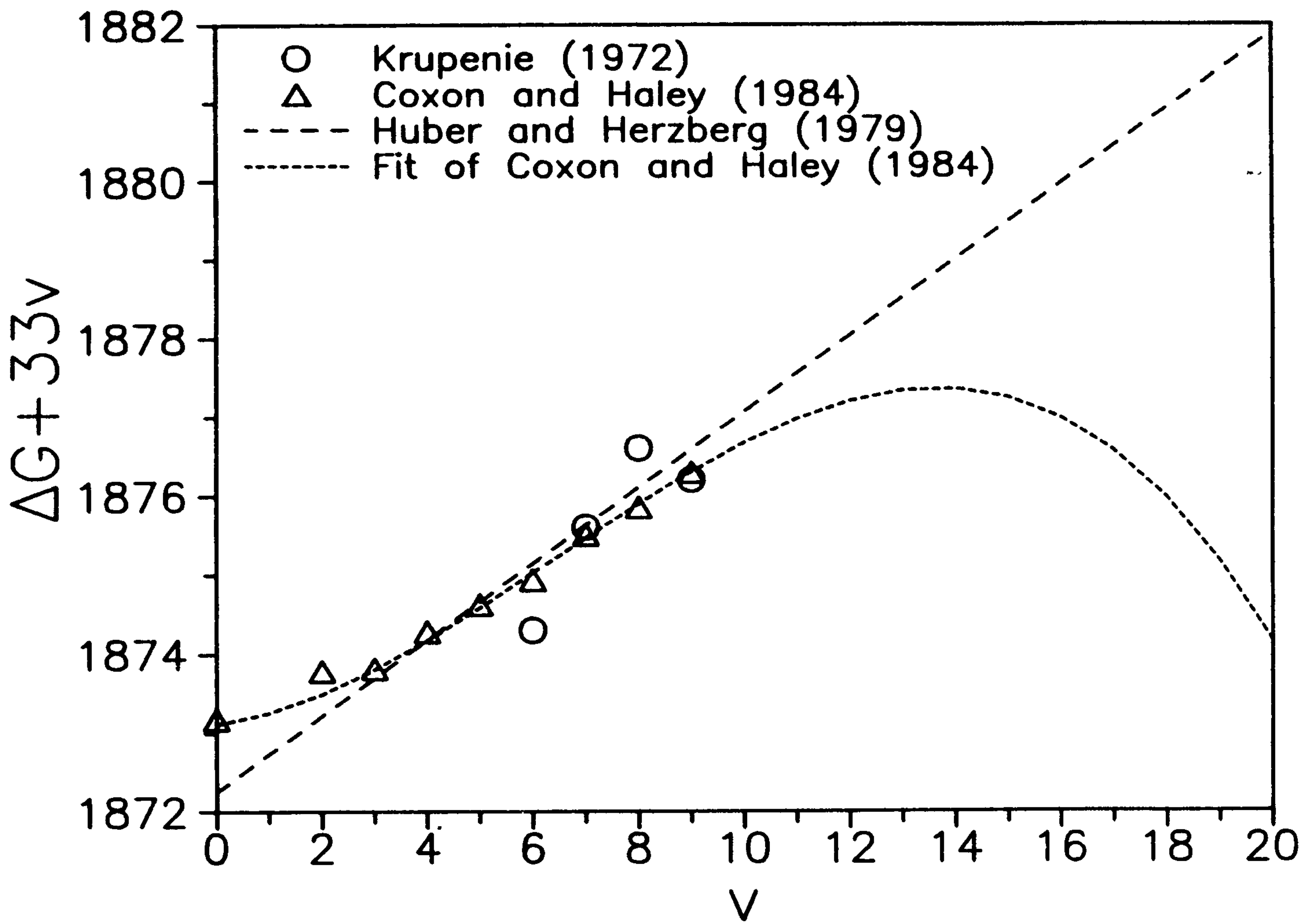

Figure 41. Vibrational data and fits for the $X\ ^2\Pi_g$ state of O_2^+.

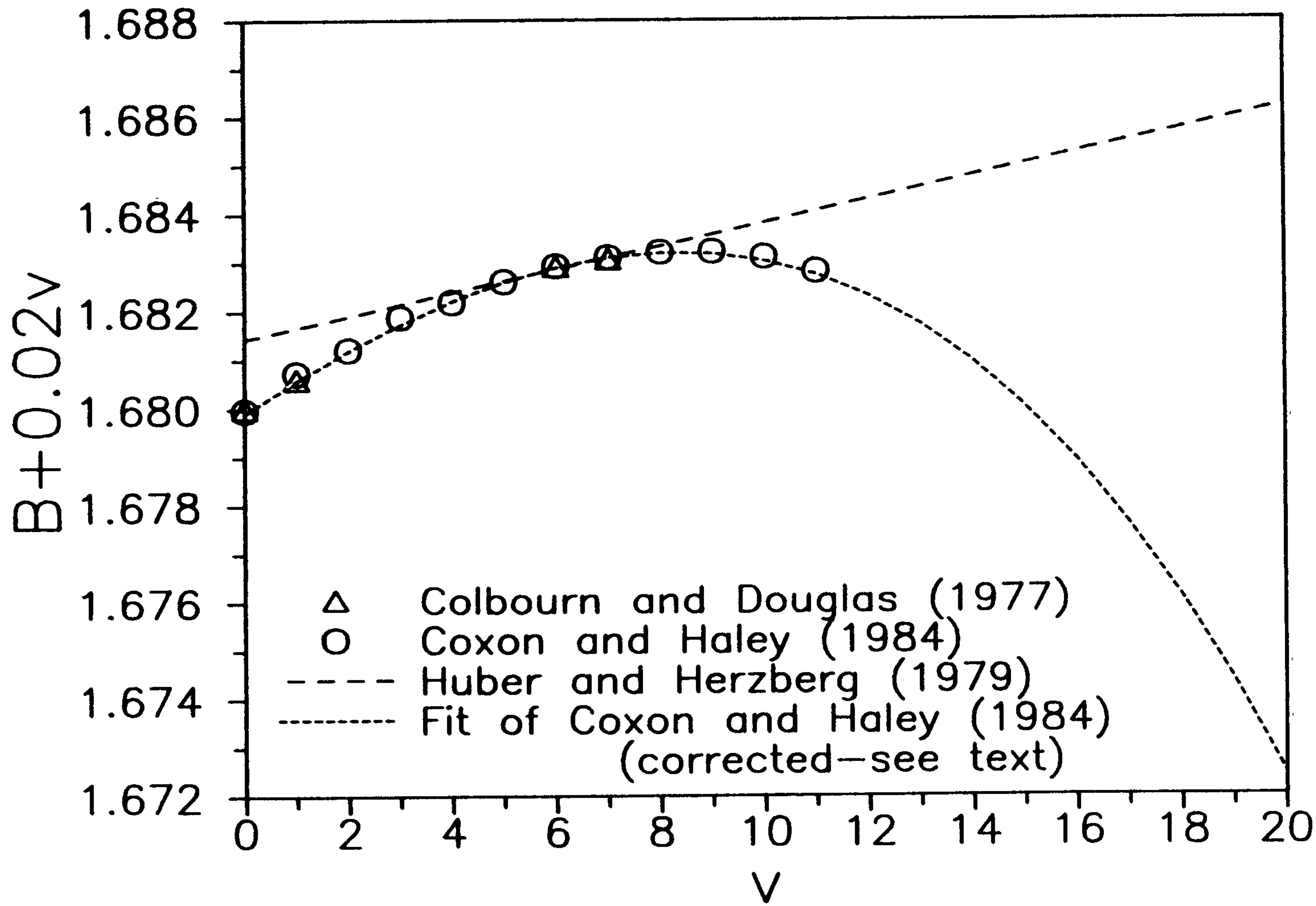

Figure 42. Rotational data and fits for the $X\ ^2\Pi_g$ state of O_2^+.

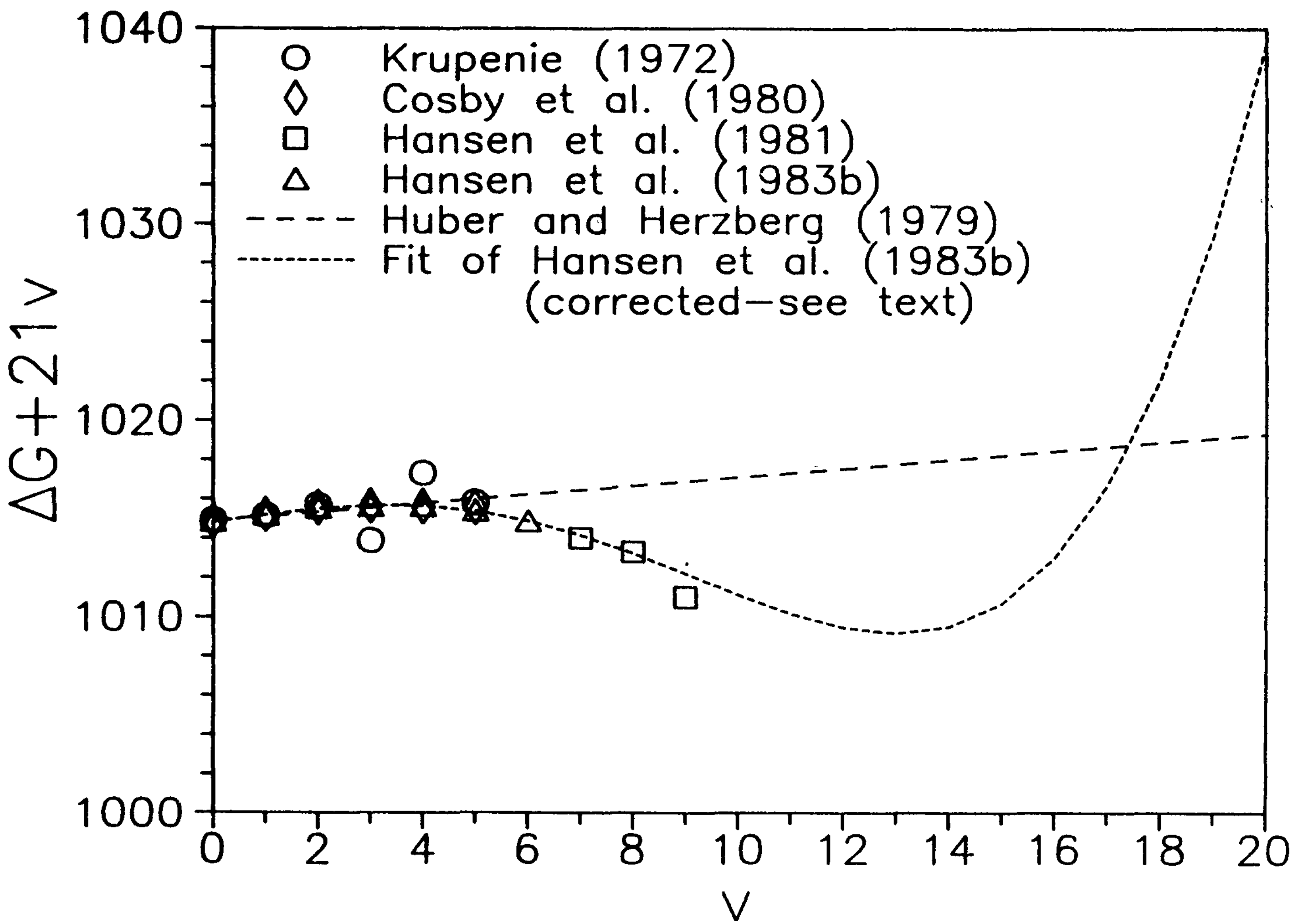

Figure 43. Vibrational data and fit for the $a\ ^4\Pi_u$ state of O_2^+.

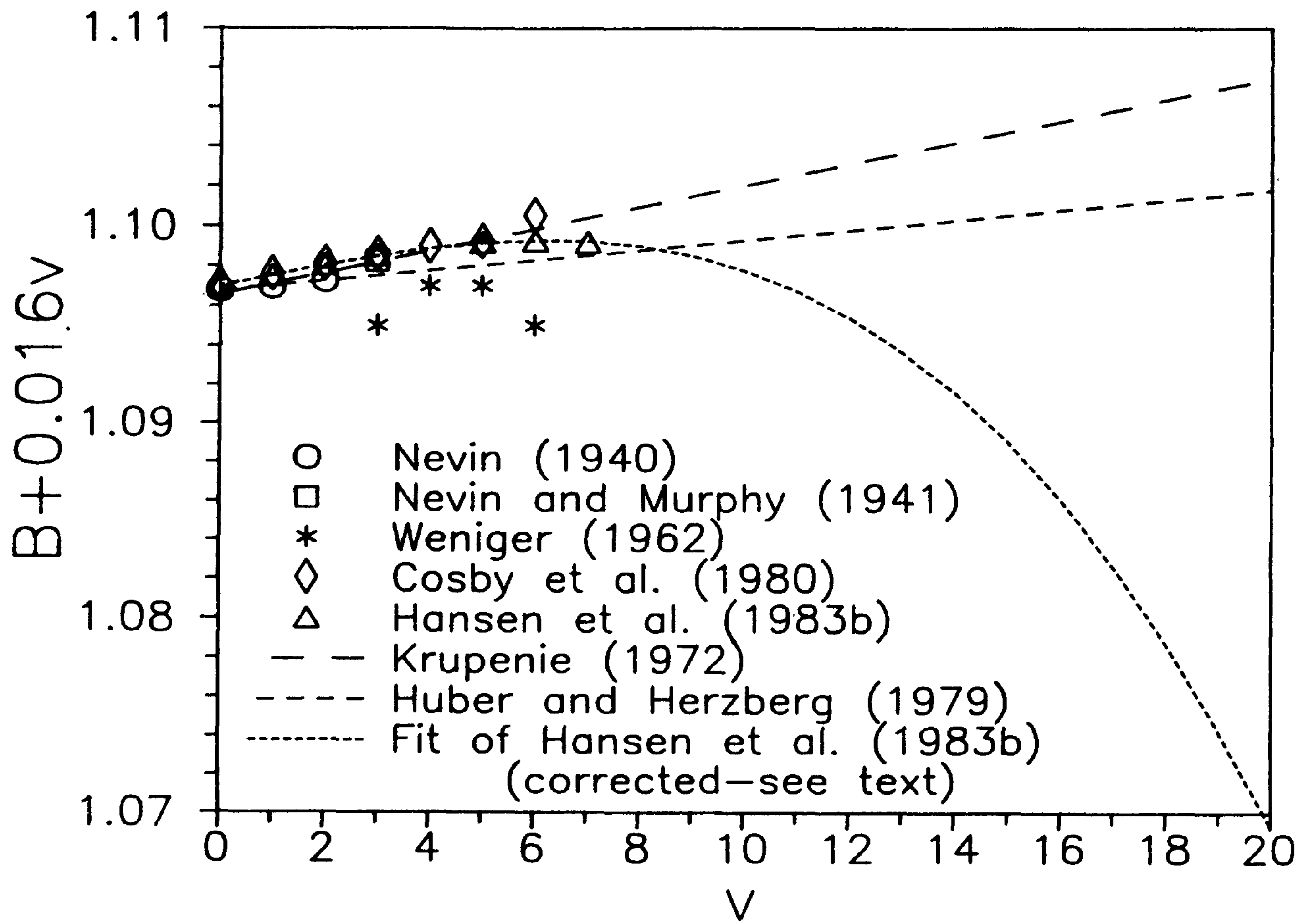

Figure 44. Rotational data and fits for the $a\ ^4\Pi_u$ state of O_2^+.

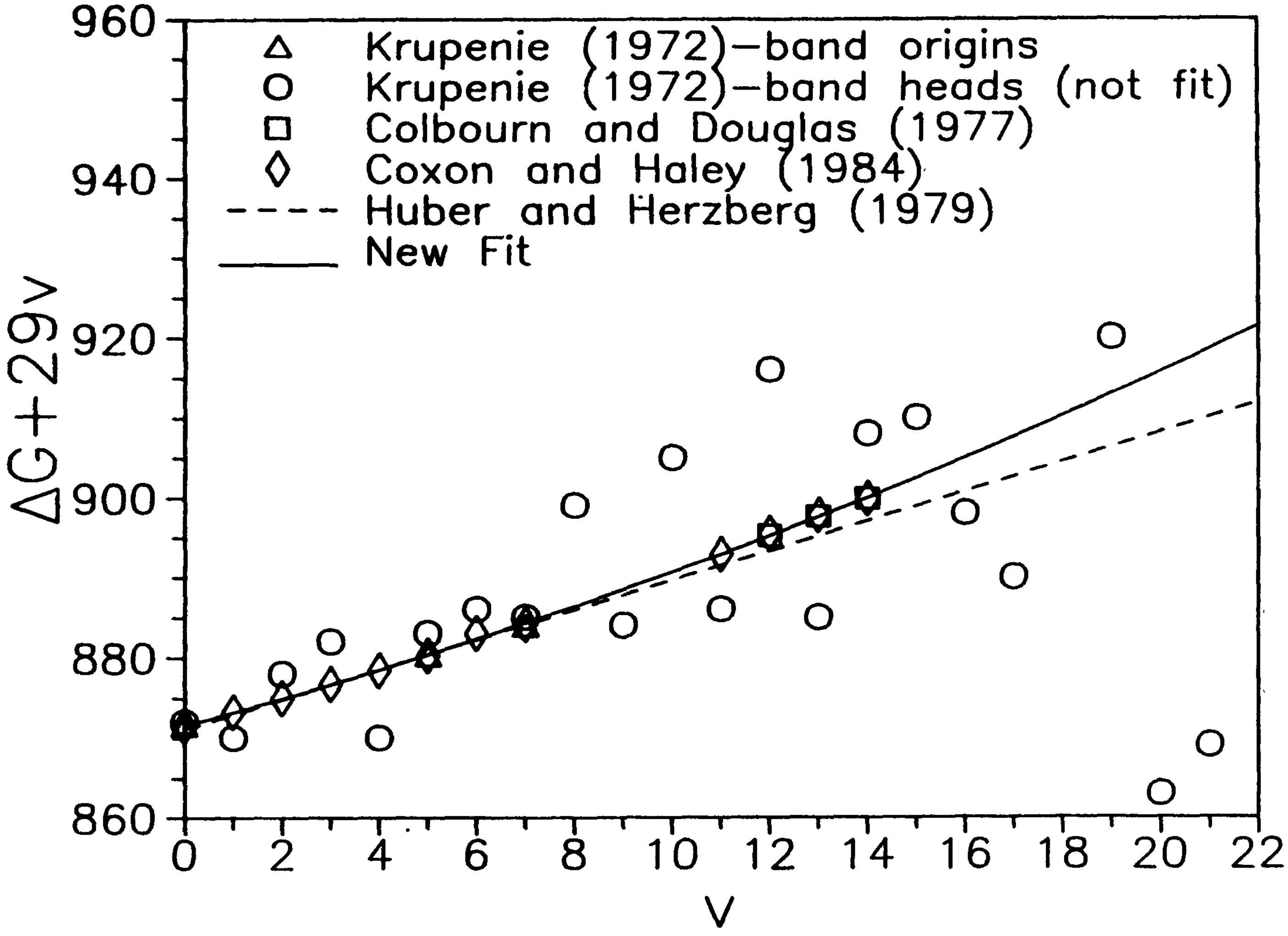

Figure 45. Vibrational data and fits for the $A\ ^2\Pi_u$ state of O_2^+.

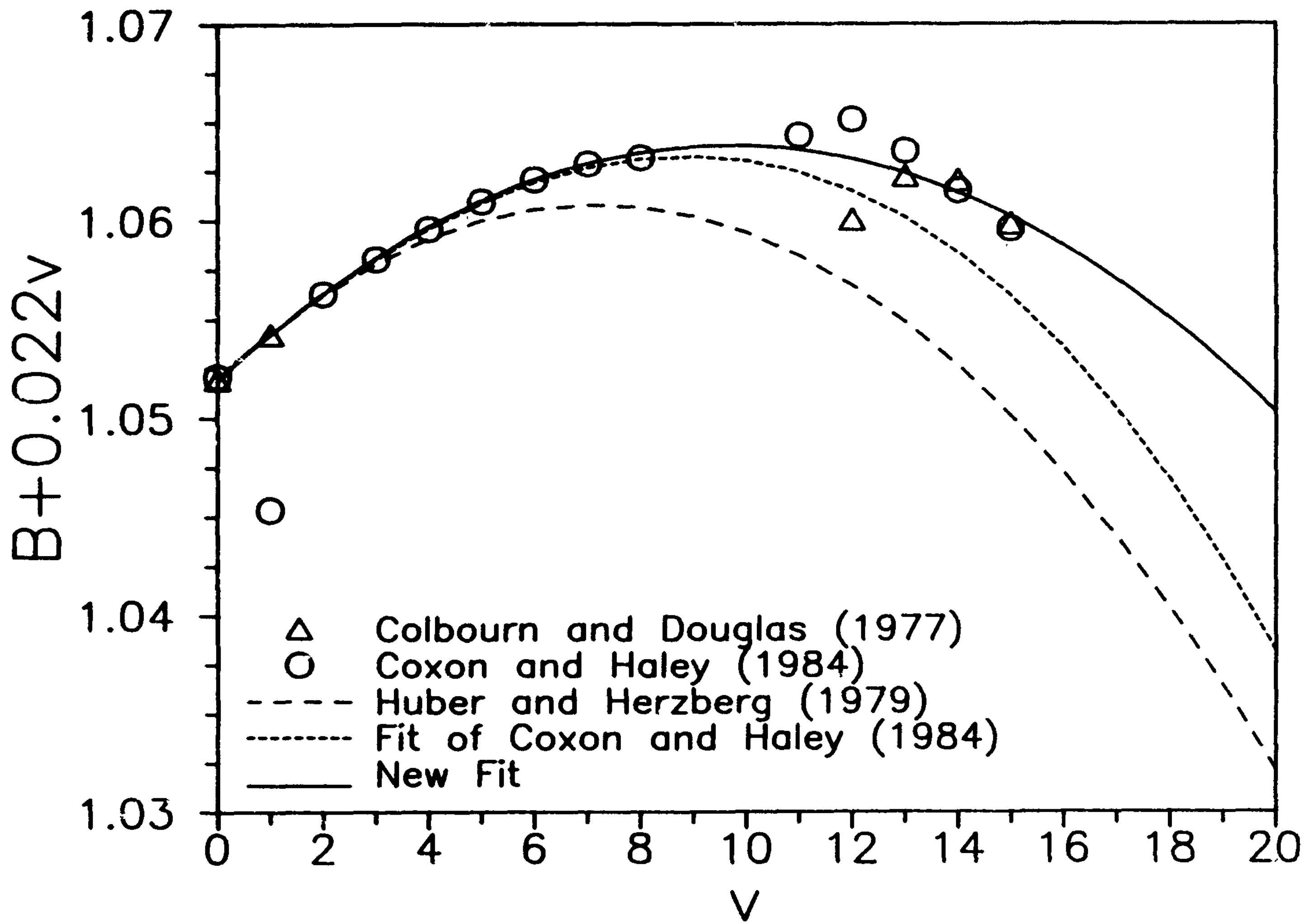

Figure 46. Rotational data and fits for the $A\ ^2\Pi_u$ state of O_2^+.

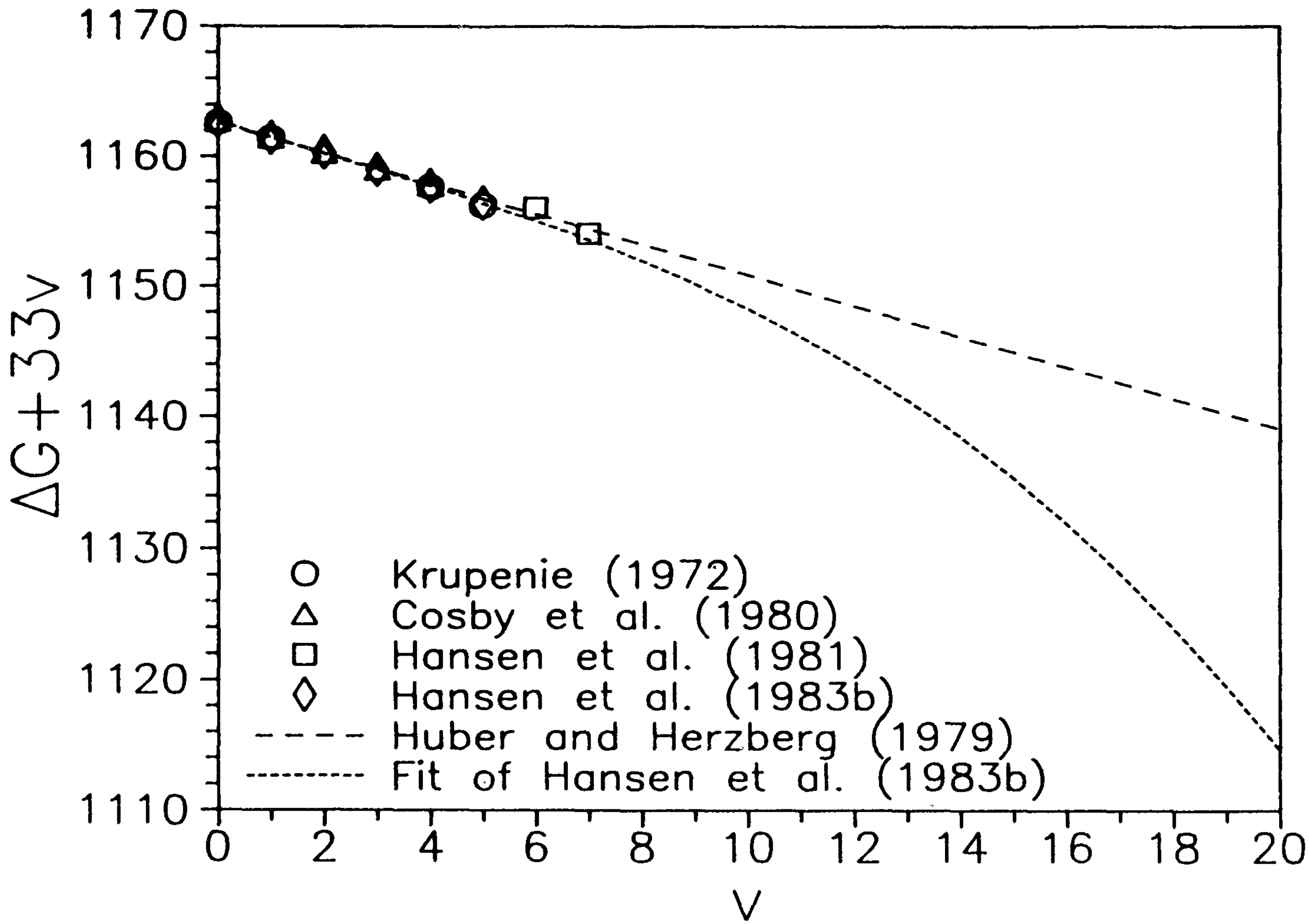

Figure 47. Vibrational data and fits for the $b\ ^4\Sigma_g^-$ state of O_2^+.

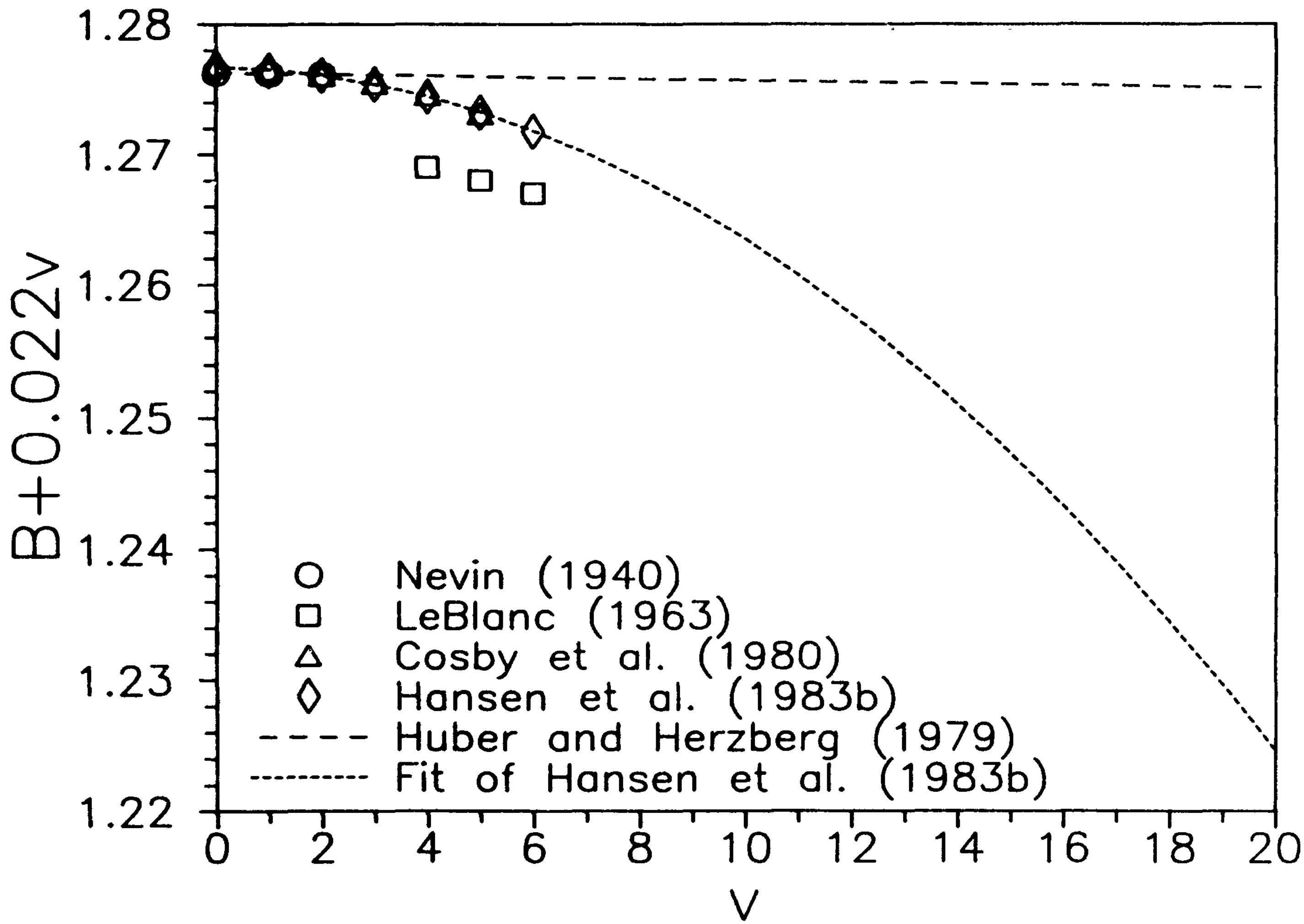

Figure 48. Rotational data and fits for the $b\,^4\Sigma_g^-$ state of O_2^+.

Table 1. Vibrational constants (cm^{-1}) of N_2 and N_2^+.

$$T_v = T_e + \omega_e(v+\tfrac{1}{2}) - \omega_e x_e(v+\tfrac{1}{2})^2 + \omega_e y_e(v+\tfrac{1}{2})^3 + \omega_e z_e(v+\tfrac{1}{2})^4 + \omega_e u_e(v+\tfrac{1}{2})^5 + \omega_e w_e(v+\tfrac{1}{2})^6$$
$$T_e = T_0 - \omega_e/2 + \omega_e x_e/4 - \omega_e y_e/8 - \omega_e z_e/16 - \omega_e u_e/32 - \omega_e w_e/64$$

	State	T_0 †	ω_e	$\omega_e x_e$	$\omega_e y_e$	$\omega_e z_e$	$\omega_e u_e$	$\omega_e w_e$
N_2^+	$C\ ^2\Sigma_u^+$	190209.5	2071.5	9.2_9	-0.43			
	$B\ ^2\Sigma_u^+$ *	151233.5	2387	7.23	-2.966	4.86(-2)‡	2.20(-3)	-5.23(-5)
	$A\ ^2\Pi_u$	134683.1	1903.7_0	15.02				
	$X\ ^2\Sigma_g^+$ *	125667.5	2206.67	16.139	-1.668(-2)	-2.152(-3)	3.195(-5)	
N_2	$y\ ^1\Pi_g$ *	114166.0	1629.8	-39.2				
	$x\ ^1\Sigma_g^-$	113212.1	1910.0	20.7				
	$c_4'\ ^1\Sigma_u^+$ *	104323.3	2175	14.4				
	$b'\ ^1\Sigma_u^+$ *	103678.3	747	3.8				
	$D\ ^3\Sigma_u^+$ *	103570.9	(2206.67)	(16.139)	(-1.668)(-2)	(-2.152)(-3)	(3.195)(-5)	
	$b\ ^1\Pi_u$ *	100816.9	596.81	-26.025	-1.8115	5.239(-2)	-7.859(-4)	
	$C'\ ^3\Pi_u$ *	97562.3	1008	106				
	$E\ ^3\Sigma_g^+$ *	95774.5	(2217.34)	(16.139)	(-1.668)(-2)	(-2.152)(-3)	(3.195)(-5)	
	$C\ ^3\Pi_u$	88977.9	2047.17_8	28.445_0	2.0883_3	-5.350(-1)		
	$w\ ^1\Delta_u$	71698.4	1559.26	11.63				
	$a\ ^1\Pi_g$	68951.2	1694.20_8	13.949_1	7.93_5(-3)	2.91(-4)		
	$a'\ ^1\Sigma_u^-$	67739.3	1530.25_4	12.0747	4.129(-2)	-2.9(-4)		
	$B'\ ^3\Sigma_u^-$	65851.3	1516.88	12.18_1	4.18_6(-2)	-7.32(-4)		
	$W\ ^3\Delta_u$ *	59380.2	1506.53	12.575	3.086(-2)	-7.071(-4)		
	$B\ ^3\Pi_g$ *	59306.8	1734.38	14.558	1.397(-2)	-1.127(-3)		
	$A\ ^3\Sigma_u^+$ *	49754.8	1460.48	13.775	-1.175(-2)	1.410(-4)	-7.292(-5)	
	$X\ ^1\Sigma_g^+$ *	0.0	2359.13	14.395	4.160(-3)	-4.374(-4)		

*The tabulated vibrational constants of this state are from a new fit to the experimental $\Delta G(v+\frac{1}{2})$ values (see text). For states not marked with an asterisk the constants given by Huber and Herzberg (1979) are found to be valid (see text) and are listed here.

†Derived from ν_{00} band origins of Huber and Herzberg (1979) and ionization potentials of Lofthus and Krupenie (1977), except for the N_2 W, B', and b' states which are from Cerny *et al.* (1980), Roux and Michaud (1988), and Verma and Jois (1984), respectively (see Section 2).

‡Read as 4.86×10^{-2}.

Table 2. Rotational constants (cm^{-1}) of N_2 and N_2^+.

$$B_v = B_e - \alpha_e(v+\tfrac{1}{2}) + \gamma_e(v+\tfrac{1}{2})^2 + \delta_e(v+\tfrac{1}{2})^3 + \epsilon_e(v+\tfrac{1}{2})^4$$

State			B_e	α_e	γ_e	δ_e	ϵ_e
N_2^+	$C\ ^2\Sigma_u^+$	*	1.5148	4.32(-3)†	-4.37(-4)		
	$B\ ^2\Sigma_u^+$	*	2.068	3.44(-3)	-4.840(-3)	2.024(-4)	-2.600(-6)
	$A\ ^2\Pi_u$	*	1.7450	1.90(-2)	-7.7(-5)		
	$X\ ^2\Sigma_g^+$	*	1.9306	1.821(-2)	-1.087(-4)	-1.44(-6)	
N_2	$y\ ^1\Pi_g$	*	1.686	-2.1(-1)	-8.3(-2)		
	$x\ ^1\Sigma_g^-$		1.750	2.25(-2)			
	$c_4'\ ^1\Sigma_u^+$	*	2.143	4.826(-1)	1.180(-1)	-8.04(-3)	
	$b'\ ^1\Sigma_u^+$	*	1.142				
	$D\ ^3\Sigma_u^+$	*	1.9701	(1.821)(-2)	(-1.087)(-4)	(-1.44)(-6)	
	$b\ ^1\Pi_u$	*	1.4396	1.123(-2)	-8.05(-4)		
	$C'\ ^3\Pi_u$	*	0.9716	-1.56(-1)			
	$E\ ^3\Sigma_g^+$	*	1.9364	(1.821)(-2)	(-1.087)(-4)	(-1.44)(-6)	
	$C\ ^3\Pi_u$		1.8247_3	1.868(-2)	-2.28(-3)	7.33(-4)	-1.5(-4)
	$w\ ^1\Delta_u$		1.498	1.66(-2)			
	$a\ ^1\Pi_g$		1.6169	1.793(-2)	$-2.9_3(-5)$		
	$a'\ ^1\Sigma_u^-$		1.4799	1.657(-2)	2.41(-5)		
	$B'\ ^3\Sigma_u^-$		1.473_3	$1.66_6(-2)$	9(-6)		
	$W\ ^3\Delta_u$	*	1.47021	1.6997(-2)	-1.01(-5)	3.3(-7)	
	$B\ ^3\Pi_g$	*	1.63802	1.8302(-2)	-8.36(-6)	-3.39(-6)	
	$A\ ^3\Sigma_u^+$	*	1.45499	1.8385(-2)	1.24(-5)	-6.72(-6)	
	$X\ ^1\Sigma_g^+$		1.99824_1	1.7318(-2)	$-3._3(-5)$		

*The tabulated rotational constants of this state are from a new fit to the experimental B_v values (see text). For states not marked with an asterisk the constants given by Huber and Herzberg (1979) are found to be valid (see text) and are listed here.

†Read as 4.32×10^{-3}.

Table 3. Vibrational constants (cm^{-1}) of O_2 and O_2^+.

$$T_v = T_e + \omega_e(v+\tfrac{1}{2}) - \omega_e x_e(v+\tfrac{1}{2})^2 + \omega_e y_e(v+\tfrac{1}{2})^3 + \omega_e z_e(v+\tfrac{1}{2})^4 + \omega_e u_e(v+\tfrac{1}{2})^5 + \omega_e w_e(v+\tfrac{1}{2})^6$$
$$T_e = T_0 - \omega_e/2 + \omega_e x_e/4 - \omega_e y_e/8 - \omega_e z_e/16 - \omega_e u_e/32 - \omega_e w_e/64$$

State		T_0 †	ω_e	$\omega_e x_e$	$\omega_e y_e$	$\omega_e z_e$	$\omega_e u_e$	$\omega_e w_e$
O_2^+ $b\ ^4\Sigma_g^-$		146556	1197.017	17.1720	1.177(-2)‡	-9.92(-4)		
$A\ ^2\Pi_u$	*	$137433._1$	899.00	13.726	1.001(-2)			
$a\ ^4\Pi_u$		$129889._3$	1035.519	10.3821	3.29(-2)	-6.37(-3)	2.18(-4)	
$X\ ^2\Pi_g$		97365	1906.07	16.5119	2.106(-2)	-7.09(-4)		
O_2 $X\ ^3\Sigma_g^-$	*	0.0	1580.41	12.1125	7.5370(-2)	-4.0913(-3)	1.3001(-4)	-2.2061(-6)

*The tabulated vibrational constants of this state are from a new fit to the experimental $\Delta G(v+\frac{1}{2})$ values (see text). For the $X\ ^2\Pi_g$ state the corrected constants of Coxon and Haley (1984) are listed (see text); for the $a\ ^4\Pi_u$ and $b\ ^4\Sigma_g^-$ states the constants of Hansen *et al.* (1983b) are listed (after correcting $\omega_e u_e$ of the $a\ ^4\Pi_u$ state).

†Derived from ν_{00} band origins of Huber and Herzberg (1979) and ionization potentials of Krupenie (1972).

‡Read as 1.177×10^{-2}.

Table 4. Rotational constants (cm^{-1}) of O_2 and O_2^+.

$$B_v = B_e - \alpha_e(v+\tfrac{1}{2}) + \gamma_e(v+\tfrac{1}{2})^2 + \delta_e(v+\tfrac{1}{2})^3 + \epsilon_e(v+\tfrac{1}{2})^4$$

State	B_e	α_e	γ_e	δ_e	ϵ_e
O_2^+ $b\ ^4\Sigma_g^-$	1.287657	2.19209(-2)†	-1.2762(-4)		
$A\ ^2\Pi_u$	* 1.06163	1.9417(-2)	-1.270(-4)		
$a\ ^4\Pi_u$	1.104758	1.5476(-2)	1.164(-5)	-5.006(-6)	
$X\ ^2\Pi_g$	1.68957	1.9300(-2)	-1.88(-5)	-1.58(-6)	
O_2 $X\ ^3\Sigma_g^-$	* 1.44504	1.5225(-2)	-8.2507(-5)	7.2494(-6)	-2.0948(-7)

*The tabulated rotational constants of this state are from a new fit to the experimental B_v values (see text). For the $X\ ^2\Pi_g$ state the corrected constants of Coxon and Haley (1984) are listed (see text); for the $a\ ^4\Pi_u$ and $b\ ^4\Sigma_g^-$ states the constants of Hansen *et al.* (1983b) are listed (after correcting γ_e of the $a\ ^4\Pi_u$ state).

†Read as 2.19209×10^{-2}.

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